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able of throwing light on the complexity of the cholesterol molecule.

The curves shown in the paper indicate that the depression on the acid side is practically linear, and in the case of palmitic acid a depression of 0·1° per g. of cholesterol in 100 g. of acid is calculated. It has been found (Stratton and Partington, *Phil. Mag.*, 1924, [vi], **48**, 1085) that the molecular depression for very pure palmitic acid (m. p. 62·25°), with mesitylene as solute, is 43·13°. A determination of the latent heat of fusion of the acid also showed that, contrary to previously recorded data, the freezing-point lowering is normally related to the latent heat.

If we now calculate the molecular weight of cholesterol from these data, we find $M = 43{\cdot}13°/0{\cdot}1° = 431$. The molecular weight calculated from the formula $C_{27}H_{46}O$ is 386. The result confirms the supposition that solid solutions are not deposited on cooling the melt.

Further experiments have been made on the depression of the freezing point of benzene, and the elevation of the boiling points of benzene and alcohol, produced by dissolved cholesterol. The latter was prepared from gall-stones by crystallisation from alcohol, had a m. p. of 148°, and was just fused before weighing out. The results obtained were as follows.

A Landsberger–Beckmann apparatus was used for the b. p. determination, redistilled Kahlbaum's benzene being used as solvent.

Expt.	G. of cholesterol.	Vol. of solution in c.c.	Elevation of b. p.	*M.*
1	0·788	15·12	0·32°	424
2	0·4288	14·7	0·225	424
3	0·8488	10·5	0·61	434
		14·28	0·46	423

(The molecular elevation per 100 c.c. is taken as 32·8 for benzene and 15·6 for alcohol.)

A b. p. determination made in pure, redistilled alcohol gave:

4	0·4749	13·65	0·127	427

The freezing-point measurements were made with the usual apparatus. The results were as follows:

Expt.	G. of cholesterol.	G. of benzene.	Obs. depression.	*M.*
1	0·333	22·709	0·178°	423
2	0·230	18·600	0·157 (2 expts.)	405

The molecular depression for benzene is taken as 51·39 per 100 g. (Stratton and Partington, *loc. cit.*).

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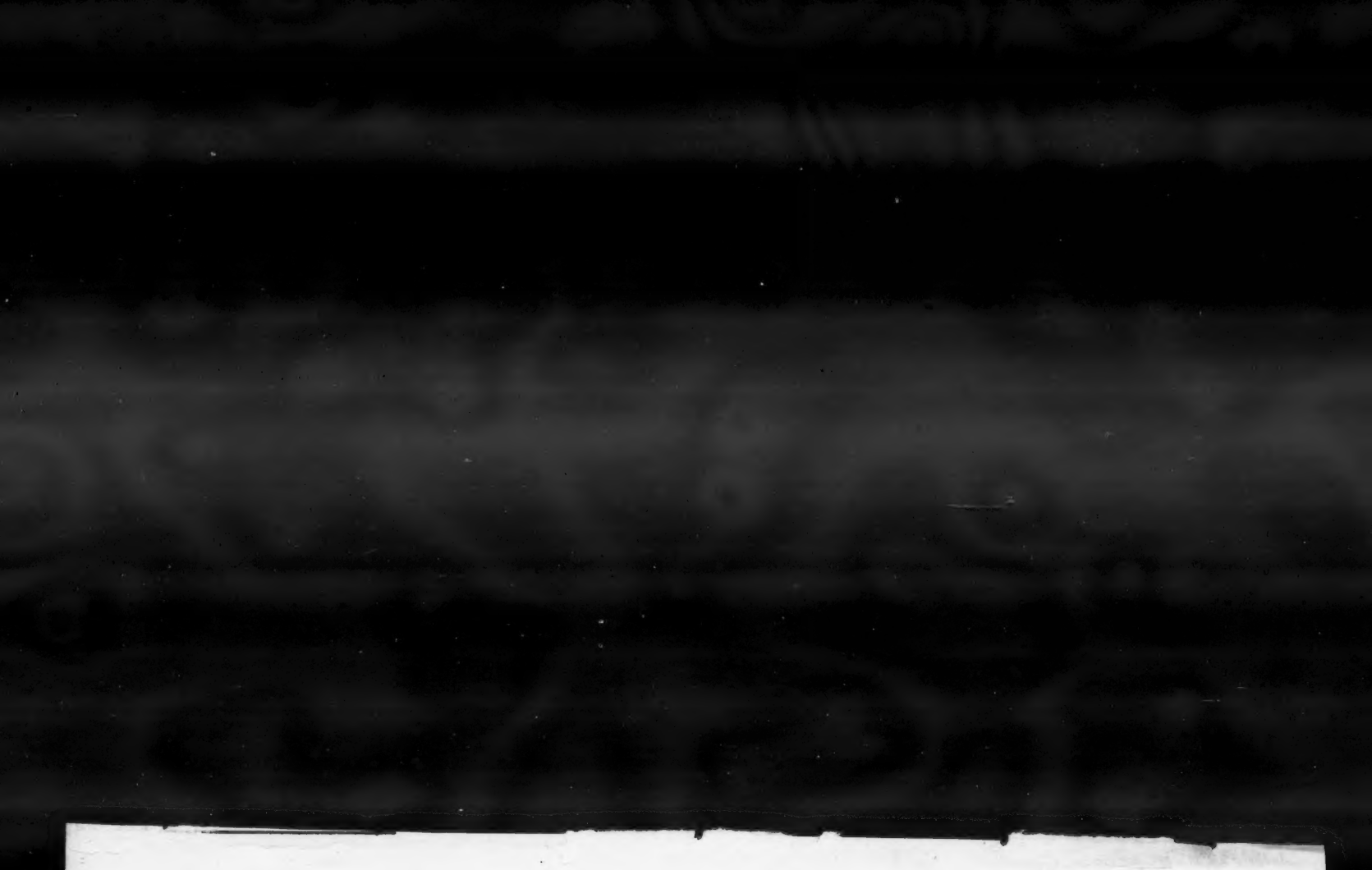


LXX.—*The Influence of Acid Concentration on the Oxidation-Reduction Potential of Cuprous and Cupric Chlorides.*

By Sydney Raymond Carter and Frederick Measham Lea.

An extended study of the oxidation potential of cuprous-cupric salts has been rendered desirable in view of the oxidising properties of sulphur dioxide towards cuprous chloride in strongly acid solution.

The reducing action of sulphur dioxide on cupric chloride in aqueous solution has long been known. The oxidation of cuprous chloride in strong hydrochloric acid solutions by sulphur dioxide has been investigated by Wardlaw and Pinkard (J., 1922, **121**, 210), who concluded that in hydrochloric acid solutions of 1·5*N* and upwards the primary reaction proceeds according to the equation $2Cu_2Cl_2 + SO_2 + 4HCl = 4CuCl_2 + 2H_2O + S$; and this process was considered to be reversible. The formation of sulphides of copper also observed was attributed to secondary reactions.

The percentage oxidation in hydrochloric acid of definite concentration was found to depend on the initial cuprous chloride concentration, the degree of oxidation being progressively greater as this concentration increased. This was explained by these workers on the basis of some results obtained by Poma (*Atti R. Accad. Lincei*, 1909, [v], **18**, i, 192), who found that, for a definite hydrochloric acid concentration, as the concentration of cupric chloride increased, the amount of cuprous chloride which could be dissolved increased enormously, whilst the number of free cuprous ions showed only a very small increase, indicating that the cuprous copper was present in the form of a complex ion. From this they inferred that, if a mixed cuprous-cupric solution be established (the potential of which would be equal to that of the sulphur dioxide at equilibrium), a greater proportion of cupric salt must be produced in the more concentrated than in the more dilute cuprous chloride solution in order that the necessary free cupric ions should be present to give the requisite oxidation potential.

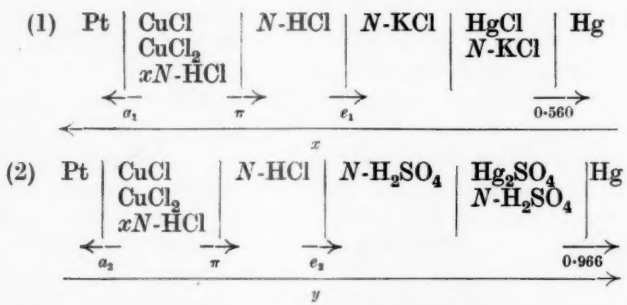
The following conventions are used in this paper. (1) Square brackets denote concentrations; thus $[Cu^{I}]$ and $[Cu^{II}]$ denote total salt concentrations, and $[Cu^{\cdot}]$ and $[Cu^{\cdot\cdot}]$ the corresponding ionic concentrations. (2) Potentials of half-electrodes are referred to the absolute scale. The following values for the *E.M.F.* of the standard half-elements have been assumed: normal calomel electrode, 0·560 volt, and the mercurous sulphate electrode (N-H_2SO_4 = 49 g. per litre), 0·966 volt. (3) For convenience, when considering com-

plete cells made up of an unknown half-element and a standard half-element, a positive sign, given to the ***E.M.F.*** of the entire cell, indicates that positive electricity is flowing from the standard half-element to the unknown through the solution.

The potential of the cuprous-cupric chloride cell was investigated by Poma (*loc. cit.*) for solutions in hydrochloric acid up to $4N$ at 25°, and no attempt was made to keep the cuprous and cupric concentrations constant, solutions, saturated with respect to cuprous chloride, being used with varying concentrations of cupric chloride. These data are therefore of little use for the present purpose, even within the limited acid region over which they extend.

An investigation was therefore carried out in which the acid concentration ranged from N to $11{\cdot}5N$ and steps were taken to correct for the diffusion potential between the standard electrode and the strong acid in the oxidation cell.

The complete cells to be investigated were of the following types :



The diffusion boundaries to be considered are π, e_1, and e_2. An alteration of the xN-HCl concentration would cause a variation of the potential π, but the potential e_1 (or e_2) would always be constant. To obtain the true variation of the oxidation potential, a_1 (or a_2), with acid concentration from the measurements of the complete cells 1 and 2, it is only necessary to know the alteration in the potential π corresponding with a change in the value of x; this was determined in a separate investigation (Carter and Lea, preceding paper, p. 487).

Experimental.

The cuprous-cupric solutions were made up with pure crystallised cupric chloride and anhydrous, white cuprous chloride, the latter being specially prepared and kept in sealed tubes until required (compare J., 1922, **121**, 210).

The cells were made up as nearly as possible to the cuprous, cupric and hydrochloric acid concentrations required and, after the

completion of the potential measurements, were analysed as follows. The cupric copper was estimated by direct titration of a known volume with titanous chloride in presence of a known amount of iron, a large excess of potassium thiocyanate being used as indicator (see Knecht and Hibbert, " New Reduction Methods in Volumetric Analysis," p. 55).

The total copper in 10 c.c. was determined by oxidising the cuprous chloride with sodium peroxide, diluting, and boiling the solution for 15 minutes; the solution was cooled, made up to 100 c.c., and an aliquot portion titrated with titanous chloride as before. The cuprous copper was thus obtained by difference. The total chloride was estimated gravimetrically, and the free hydrochloric acid calculated.

Precautions were taken to prevent oxidation of the cuprous chloride by air while the preparation of the cells, the potential measurements, and the subsequent analysis were in progress. The solutions were maintained in an atmosphere of nitrogen throughout these operations. Two or more indifferent electrodes of platinised platinum were used in each cell and identical values were always obtained. All measurements were made at 18°.

Liquid Connexions.—Liquid connexion with the cuprous-cupric element was made by tubes, fitted with taps, filled with the cell electrolyte and dipping into a similar solution. Connexion between this xN-hydrochloric acid and the N-hydrochloric acid was made by inverted **U**-tubes filled with N-hydrochloric acid. These tubes were about 3 mm. in bore, and the ends were plugged with filter-paper. Liquid connexion between the N-hydrochloric acid and the standard half-element was made in a similar manner, the **U**-tube in this case, however, being filled with the standard half-element electrolyte.

Influence of Acid Concentration.—A series of cells was examined in which the acid concentration varied from N to $11{\cdot}5N$. The cuprous and cupric chloride concentrations were as nearly as possible the same and equal to $0{\cdot}1N$, the total copper concentration thus being $0{\cdot}2N$. (*Note.*—A " normal solution " signifies one gram-atom, 63·57 grams of copper per litre.) The results were subsequently corrected to the ratio $[Cu^{I}]/[Cu^{II}] = 1{\cdot}000$ by means of the logarithmic formula

$$E = E_0 - RT/nF.\ \log\ [Cu^{I}]/[Cu^{II}].$$

The correction to be applied was never greater than 0·001 volt in this series, and its average value was about 0·0005 volt.

Cell 1 was subject to slight fluctuation (up to 0·0015 volt) on keeping, but cell 2 remained almost constant. This was un-

doubtedly due to fluctuation in the diffusion potential set up at the N-HCl|N-KCl boundary; the N-HCl|N-H_2SO_4 boundary remained without appreciable alteration. For this reason, the potentials against the mercurous sulphate electrode are probably more trustworthy than those against the calomel electrode.

In this way, the *E.M.F.*'s of the entire cell, which are denoted by x and y in cells 1 and 2, respectively, were obtained and the results are given in Table I. Acid concentrations are recorded in gram-equivalents per litre.

TABLE I.

Series X. $[Cu^I] = [Cu^{II}] = 0{\cdot}1N$.

	E.M.F. (volt).			*E.M.F.* (volt).	
[HCl].	x.	y.	[HCl].	x.	y.
11·67	+0·2047	−0·1802	4·63	+0·2276	−0·1579
9·23	0·2160	0·1683	3·99	0·2159	0·1670
7·74	0·2241	0·1601	2·97	0·1977	0·1863
6·77	0·2282	0·1557	2·03	0·1781	0·2073
6·12	0·2307	0·1549	1·39	0·1592	0·2248
5·56	0·2282	0·1563			

It is seen that the cuprous-cupric potential has a maximum value in about 6N-acid.

A further series, Z, consisting of cells in which the cuprous and cupric chloride concentrations were 0·025N, was similarly examined.

TABLE II.

Series Z. $[Cu^I] = [Cu^{II}] = 0{\cdot}025N$.

	E.M.F. (volt).			*E.M.F.* (volt).	
[HCl].	x.	y.	[HCl].	x.	y.
11·56	+0·2011	−0·1831	6·37	+0·2302	−0·1556
10·35	0·2081	0·1766	5·89	0·2289	0·1556
9·86	0·2118	0·1712	5·07	0·2251	0·1580
8·01	0·2221	0·1617	3·48	0·2105	0·1742
7·80	0·2251	0·1594	3·39	0·2093	0·1761
7·39	—	0·1584	2·49	0·1866	0·1981
6·50	0·2296	0·1558	1·545	0·1627	0·2229

It is obvious from comparison with Table I that, over the range of acid concentration investigated, the potentials for low copper concentrations are independent of the total copper concentration. Curves of potential against acid concentration are almost identical and superimposable.

Corrections for Diffusion Potential and Calculation of Absolute E.M.F.—Referring to the cells of types 1 and 2, the points of potential difference and their direction of action have been indicated.

The potentials x and y of the complete cells as obtained from Series X, Table I, will be employed. The values of π are taken from the preceding paper. The potentials e_1 and e_2, calculated,

on the basis of Henderson's formula (*Z. physikal. Chem.*, **1907, 59**, 118), from conductivity data are 0·0288 volt and 0·0065 volt, respectively.

Consider cell 1 and let the potential of the half-element (Pt)|CuCl,$CuCl_2$,xN-HCl be a_1. If the total *E.M.F.* of the complete cell be x, then a_1 (volts) $= x + \pi + 0{\cdot}0288 + 0{\cdot}560$. Similarly for cell 2, if a_2 denotes the *E.M.F.* of the half-element (Pt)|CuCl,$CuCl_2$,xN-HCl as obtained from cell 2, then $a_2 = y + \pi + 0{\cdot}0065 + 0{\cdot}966$.

The results are tabulated below, and for convenience the acid concentrations are given in whole numbers, the values of x and y being taken from curves plotted from Series X, Table I.

TABLE III.

	E.M.F. (volt).				
[HCl].	x.	y.	π.	a_1.	a_2.
1·0	+0·149	−0·236	0·0000	0·7378	0·7365
2·0	0·1766	0·2075	0·0163	0·7814	0·7813
3·0	0·1988	0·1850	0·0296	0·8172	0·8171
4·0	0·2159	0·1675	0·0400	0·8447	0·8450
5·0	0·2256	0·1576	0·0505	0·8649	0·8654
6·0	0·2301	0·1545	0·0591	0·8780	0·8771
7·0	0·2272	0·1565	0·0674	0·8834	0·8834
8·0	0·2227	0·1618	0·0726	0·8841	0·8833
9·0	0·2176	0·1669	0·0770	0·8834	0·8826
10·0	0·2126	0·1720	0·0806	0·8820	0·8811
11·0	0·2075	0·1772	0·0839	0·8802	0·8792
11·5	0·2050	0·1798	0·0853	0·8791	0·8780

The agreement between the values of a_1 and a_2 for the cuprous-cupric potential as calculated from measurements against calomel and mercurous sulphate half-element readings, respectively, is satisfactory. The maximum value of a_1—a_2 is of the same order as might be introduced by variation of the diffusion potential e_1.

The values of a_2 are shown plotted against acid concentration in curve 1 (Fig. 1). It is seen that for acid above 6N there is very little change in the cuprous-cupric potential.

Discussion of the Causes of the Changes in Oxidation Potential due to Acid Concentration.—The general form of the curve of the cupric-cuprous potential (curve 4, Fig. 1) is very different from that of the ferric-ferrous chlorides (J., 1924, **125**, 1883). In the former case, however, one of the components, cuprous chloride, is almost insoluble in water, but soluble in hydrochloric acid. Moreover, the solubility increases with rise in acid concentration (Engel, *Ann. Chim. Phys.*, 1889, **17**, 376). The cuprous chloride in the solution must therefore be in the form of complex salts or ions, formed by combination with the hydrochloric acid, and consequently the concentration of cuprous ion will be exceedingly small.

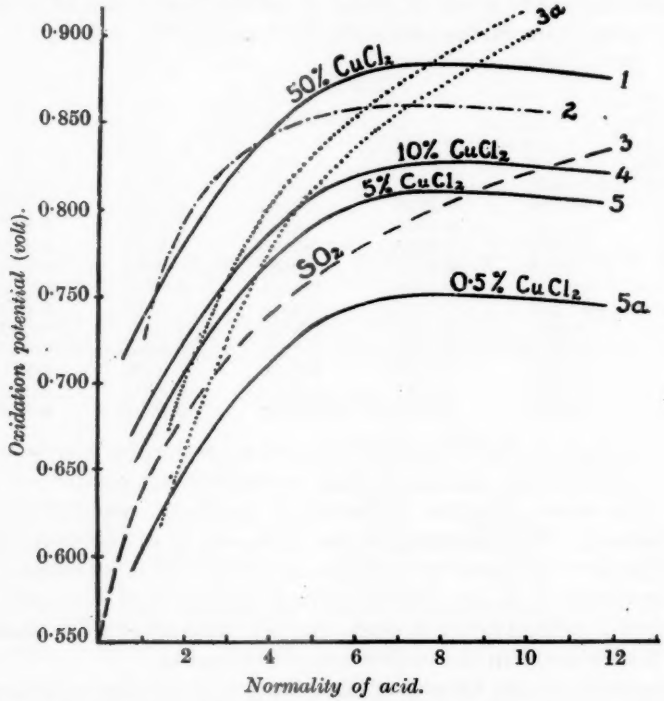
(*a*) The cupric-cuprous potential curve shows a maximum at 7*N*—8*N*, which is approximately the same acid concentration as the maximum in the ionic concentration curve for hydrochloric acid in Table IV as calculated from Green's formula,

$$[Cl'] = \alpha\,[HCl] = (\Lambda_v/\Lambda_\infty)\,(\eta_v/\eta_0)^{0\cdot55}\,[HCl]$$

(J., 1908, **93**, 2023. The conductivity data are taken from Kohlrausch and Holborn, "Leitvermögen der Elektrolyte," 1898, pp.

FIG. 1.

Oxidation potentials of cupric and cuprous chlorides in hydrochloric acid.



154, 160, and the viscosity data from Landolt-Börnstein "Tabellen," 1912, p. 83, and Taylor and Ranken, *Proc. Roy. Soc. Edin.*, 1904, **25**, 231—241).

TABLE IV.

[HCl] ...	1·00	2·00	3·00	4·00	5·00	6·00	7·00	8·00	9·00	10·00
[H·] or [Cl']	0·82	1·42	1·83	2·12	2·30	2·38	2·39	2·37	2·35	2·32

This may be explained by the fact that cuprous chloride and hydrogen chloride are known to form compounds $H_2Cu_2Cl_4$ and H_2CuCl_3, which would give rise to the ions Cu_2Cl_4'' and $CuCl_3''$,

the formation of the latter being the more likely in strong hydrochloric acid solution (Bodländer and Storbeck, *Z. anorg. Chem.*, 1902, **31**, 1; Noyes and Chow, *J. Amer. Chem. Soc.*, 1918, **40**, 739).

Assuming the existence of the compound H_2CuCl_3 in solution, it may be shown that $[Cu^{\cdot}] = k[Cl']^5$ and hence $E = E_0 + 0{\cdot}058 \log [Cl']^5$, where E_0 is the value when $[Cl'] = 1{\cdot}00$.

The values of E which have been calculated from this equation by means of the data for [Cl'] recorded in Table IV are plotted in curve 2 (Fig. 1) for comparison with the cupric-cuprous potential (curve 1) based on values given in Table III.

The two curves show a close resemblance, but the agreement may to a certain extent be accidental, since there are two weak points involved in the above deductions. It is questionable whether the [Cl'] could be deduced accurately from conductivity–viscosity data for concentrated hydrochloric acid solutions. Moreover it is doubtful whether the law of mass action would apply in such an instance.

(*b*) It is also possible that considerable complex formation may take place in solution between cupric chloride and hydrogen chloride, since, at 0°, Foote identified a solid compound, $CuCl_2,HCl,3H_2O$, in acid of concentration above 31% (*J. Amer. Chem. Soc.*, 1923, **45**, 663). In this case, free cupric chloride would be removed thus :

$$CuCl_2 + n\text{HCl} = CuCl_2,n\text{HCl}.$$

Consequently, with increasing [HCl], the [Cu$^{\cdot\cdot}$] would be diminished according to the equation

$$CuCl_2 = Cu^{\cdot\cdot} + 2Cl'.$$

This would result in a steady diminution in *E.M.F.* with rise in [HCl] such as is observed in the ferric-ferrous potentials, and would produce an effect opposed to that described in the previous paragraph (*a*).

Probably both factors are operating. At low acid concentrations, the changes in cuprous ion outlined in (*a*) are producing the rise in potential, whilst at high acid concentrations the changes in cupric ion indicated in (*b*) come into play, a maximum being produced in about 7*N*- to 8*N*-hydrochloric acid.

Complex Formation between Cuprous, Cupric, and Hydrogen Chlorides.—On adding a green solution of cupric chloride in hydrochloric acid to a colourless solution of cuprous chloride, also in hydrochloric acid (or even to white, solid cuprous chloride), a dark brown compound was at once formed and for high copper concentrations the solution so obtained was extremely dark in colour. The formation of this complex also appears to be dependent on the chlorine-ion concentration, since, for a given series, such as X,

the colour of the solution (in which $[Cu^{I}] = [Cu^{II}] = 0{\cdot}1N$) changed from light green to yellow-brown on increasing the acid concentration.

The production of this brown compound was also observed by Poma (*loc. cit.*), who states that, on electrolysis, it migrates to the anode and hence must be negatively charged. The constitution of this complex is unknown, but its formation will obviously lead to deviations from the above fifth-power relation.

The Applicability of the Logarithmic Law.—In view of the large degree of complex formation that occurs in solutions of the copper chlorides in hydrochloric acid it was doubtful whether the logarithmic law for changes in the cuprous-cupric ratio would hold, and therefore a series of cells was made at constant acid concentration with varying proportions of cuprous and cupric chlorides. In the following series (A), the total copper concentration was approximately equal to $0{\cdot}2N$, whilst the acid concentration in all cases was $9{\cdot}0N$. Row 2 shows the observed *E.M.F.* of the cell complete with a standard calomel half-element. Row 3 shows the value of the normal potential, E_0, as obtained from the data in row 2 by the formula $E_0 = E + RT/F \,.\, \log [Cu^{I}]/[Cu^{II}]$ after correcting for all diffusion potentials and allowing for the calomel electrode.

TABLE V.

Series A. $[HCl] = 9{\cdot}0N$.

1	$[Cu^{I}]/[Cu^{II}]$	0·1314	0·348	1·000	6·93	21·95	27·65
2	E (calomel). Volt.	0·2628	0·2441	0·2179	0·1680	0·1432	0·1380
3	E_0. Volt.	0·8775	0·8833	0·8837	0·8825	0·8869	0·8875

From the values of E_0 it is seen that the logarithmic law holds fairly closely, but that the deviations from it become appreciable when extreme ratios are considered. In order to test this for other acid concentrations, further measurements in $6{\cdot}17N$-hydrochloric acid were carried out. Two cells were measured, with $[Cu^{I}]/[Cu^{II}]$ equal to 1·00 and 0·3143, respectively. The observed change in potential was 0·0273 volt, while that demanded by direct application of the logarithmic law is 0·029 volt. The deviation is again small, and hence over moderate ratio changes the logarithmic law may be applied with little error.

Effect of Total Copper Concentration.—A further series (C) of cells was investigated, high concentrations of the copper chlorides being used, to test the general effect of high total copper concentration on the potential. Considerable difficulty was encountered in making the potential measurements. Fluctuations of the *E.M.F.* up to 0·005 volt took place, according to the degree of mixing which occurred at the aN-CuCl,bN-$CuCl_2$,xN-HCl|N-HCl liquid boundary. This was ascribed to the influence of the high copper

concentrations, since, under these conditions, the current across the boundary would not be carried in its entirety by the hydrogen and chlorine ions, as would be the case with the very low copper concentrations previously employed. It is a similar effect in a more marked degree to that already found obtaining in the case of the KCl|HCl boundary. In all cases, the initial potential values measured after making first contact and obtaining a sharp boundary were used, as these were the most consistent and reproducible of all the results obtained.

The results obtained in this series (C) are given in Table VI. The total copper concentrations were high in all cases, but were not kept constant as hitherto. The acid concentration was 8·45*N*. Column 4 shows the *E.M.F.* of the cell complete with a calomel half-element. Column 5 shows the value of E_0 obtained from data recorded in column 4, after correction for all diffusion potentials as before.

TABLE VI.

Series C. [HCl] = 8·45*N*.

[Cu^{I}].	[Cu^{II}].	[Cu^{I}]/[Cu^{II}].	ϵ (volt).	E_0 (volt).
0·099	1·112	0·089	0·2874	0·8896
0·698	1·175	0·594	0·2413	0·8915
0·905	0·958	0·945	0·2326	0·8945
1·925	0·350	5·50	0·1896	0·8959
2·78 *	0·122	22·84	0·1611	0·9031

* This cell contained a saturated solution of cuprous chloride.

The values of E_0 given in column 5 show that, even for concentrated solutions, the deviations from the logarithmic law are comparatively small, though they become appreciable when extreme ratios are considered and when the cuprous chloride concentration begins to approach the saturation point.

The general conclusion may be drawn, from Series A and C, that the logarithmic law is roughly applicable for changes in the cuprous-cupric ratio, for any concentration of total copper and acid, over moderate ranges, but does not hold when very large ratios are considered.

Action of Sulphur Dioxide on Cuprous and Cupric Salts.

(a) *Influence of Acid Concentration.*—The cuprous-cupric potentials when [Cu^{I}] = [Cu^{II}] = 0·1*N*, as given in Table III, are plotted in curve 1, Fig. 1.

The potentials for mixtures containing 10·0, 5·0, and 0·5% of cupric-copper have been deduced by the logarithmic formula $E = E_0 + 0{\cdot}058 \log [Cu^{II}]/[Cu^{I}]$ and are shown in curves 4, 5, and 5*a*, respectively.

The limiting ratio for which the logarithmic formula holds is

practically 5% and the potential for the 0·5% mixture is therefore somewhat higher. The sulphur dioxide oxidation potential as obtained by Carter and James (J., 1924, **125**, 2231) is plotted against acid concentration in curve 3. Too much reliance, however, should not be placed on this curve, as the potentials refer to a process which is probably not strictly reversible. The band 3*a* indicates the region in which sulphur dioxide is neither reduced nor oxidised, as inferred from the ferrous-ferric salts (Carter and Clews, J., 1924, **125**, 1887). The *E.M.F.'s* on this diagram are on the absolute scale and have been corrected for diffusion potentials. The values are therefore somewhat higher than in the corresponding figure for the ferrous–ferric salts, in which the diffusion potential has not been eliminated. Any cuprous-cupric mixture in a mixture of definite concentration will establish a certain oxidation-reduction potential, and the magnitude of this potential compared with that required for the reduction of sulphur dioxide will determine the amount of reaction which takes place and its direction. When these two potentials are equal, a condition of equilibrium will exist; and, in general, reaction will occur until this state is established.

An inspection of the curves indicates that cupric chloride should be reduced to a certain extent by sulphur dioxide in concentrated acid solution, although the reaction would not proceed to completion. This is in accordance with the experiments of Wardlaw and Pinkard (J., 1922, **121**, p. 217, Tables V and VI). In faintly acid solution also, reduction should occur, but even here the reaction would probably be incomplete; for example, when cuprous chloride prepared by the reduction of cupric chloride with sulphur dioxide is being washed with dilute sulphur dioxide solution the liquor invariably has a blue tinge. Nevertheless a colourless specimen of the cuprous chloride can be obtained if the cupric salt is removed by rapid filtration. A considerable portion of the sulphur dioxide curve lies above the cuprous curve (cupric/cuprous= 0·5/99·5) and in such cases sulphur dioxide acts as an oxidising agent towards cuprous salts. Between *N*- and 4*N*-acid the difference is slight and the percentage oxidation to be expected is small. Over part of this range cuprous sulphide also is formed, but the main factor regulating the reaction is evidently the difference in potential between the cuprous-cupric chloride and the sulphur dioxide (Wardlaw and Pinkard, *loc. cit.*, p. 215, Table III, exp. 13—18; p. 216, Table IV).

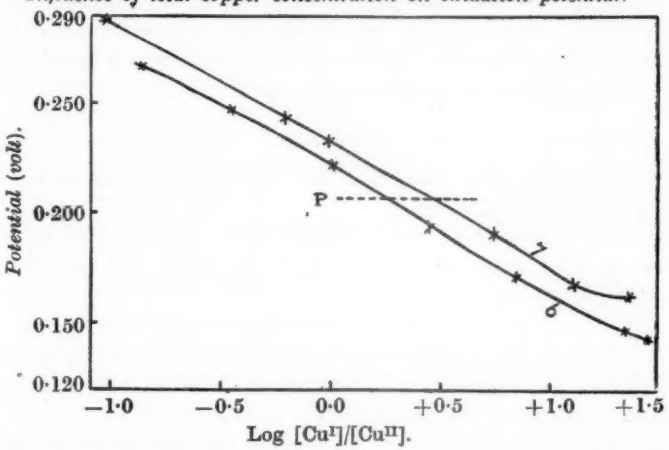
At an acid concentration of 6*N* the cuprous and sulphur dioxide potential curves diverge considerably, hence for 6*N*-acid and upwards the tendency for cuprous chloride to be oxidised by sulphur dioxide increases (*loc. cit.*, p. 215, Table III, exp. 10 and 11).

Since 6 is approximately the normality of the constant-boiling mixture of hydrogen chloride and water, this is the prevailing mixture; in the earlier stages, however, before the excess of hydrogen chloride has been driven off, the acid would be stronger than this for a time.

(b) *Influence of Copper Concentration.*—Reference has already been made to the effect of initial cuprous chloride concentration on the degree of oxidation obtained and also to the theory advanced to explain it.

FIG. 2.

Influence of total copper concentration on oxidation potential.



Curves 6 and 7 (Fig. 2) have been plotted from the A and C series of experiments given in Table V, row 2 and Table VI, column 4, respectively, in which the acid concentration was maintained constant while the cuprous-cupric ratio was varied. Both curves have been corrected to the same acid concentration (8·45*N*), and hence curve 7 gives the potential for any given cuprous-cupric ratio, when the total copper concentration is large (>1·5*N*), whilst curve 6 gives the corresponding potential when the total copper concentration is low (0·2*N*). Curve 7 shows a uniformly higher potential than curve 6 for any given cuprous-cupric ratio. Therefore to obtain any given potential *P* (see curves), a higher proportion of cupric copper is necessary in the case of the low total copper concentration than in the case of the high total copper concentration. This result is not in agreement with the theory advanced by Wardlaw and Pinkard (*loc. cit.*) to account for the fact that the percentage oxidation is progressively higher as the initial concentration of cuprous chloride increases, the actual effect of the total copper concentration on the cuprous-cupric potential

being the reverse of that which they postulated. The potential differences involved between corresponding points on curves 6 and 7 are, however, comparatively small. It is obvious that some other reason must be sought to account for their results and also to explain why the effect observed by these workers is contrary to that demanded by the oxidation-reduction potentials concerned. It will be noted that in the oxidation experiments sulphur dioxide was allowed to pass for 4 hours only and the oxidation values obtained were not expected to be true equilibrium values. In these circumstances, the velocity of the reaction would be one of the main factors determining the degree of oxidation obtained. It is curious, however, that in the analogous case of the chlorides of iron the initial ferrous chloride concentration has a much smaller effect on the degree of oxidation obtained.

Summary.

The cuprous-cupric potential and the various factors affecting it have been investigated.

The true variation in the potential with alteration of acid concentration has been obtained after correction for all diffusion potentials involved.

A theoretical explanation of these changes has been given.

The effect of the cuprous-cupric ratio on the potential has been studied and the logarithmic law shown to hold as a fair approximation over moderate ranges of change in this ratio.

The results have been used to explain the oxidation of cuprous chloride by sulphur dioxide.

The authors desire to express their thanks to the Advisory Council of the Department of Scientific and Industrial Research for a grant to one of them (F. M. L.) which has enabled him to participate in this investigation.

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[*Received, November 26th*, 1924.]

LXXI.—*The Action of Light on Chlorine Dioxide.*

By HENRY BOOTH and EDMUND JOHN BOWEN.

WHEN gaseous chlorine dioxide is exposed to light, a large quantity of a red liquid forms on the walls of the vessel (Bowen, J., 1923, **123**, 2328). The photochemical decomposition, therefore, is not that usually represented in text-books :

$$2ClO_2 \longrightarrow Cl_2 + 2O_2.$$

The present paper is an account of experiments to determine the nature of the substances produced. Most of the work was done with chlorine dioxide–carbon dioxide mixtures prepared by Bray's method (*Z. physikal. Chem.*, 1906, **54**, 463) on account of the ease of manipulation, and of the freedom from chlorine of the product, but it was proved that similar results were obtained with chlorine dioxide prepared by the much more dangerous potassium chlorate–sulphuric acid process. The gases were dried with phosphorus pentoxide and passed into evacuated glass vessels fitted with taps, which were lubricated sometimes with vaselin and sometimes with phosphoric acid.

On continued exposure to light, the red liquid first obtained from chlorine dioxide becomes colourless. The reaction occurs in the absence of moisture. It was found possible to seal the gas in small glass bulbs, if it were displaced from the capillary leading-in tubes before sealing. Such bulbs containing phosphorus pentoxide as drying agent were kept for 8 weeks in the dark; on exposure, the liquid was produced as in experiments in which the drying had not been so thorough. The pressure in the vessel diminishes during the change.

The liquid boils at about 80° at the ordinary pressure. It dissolves in water with evolution of heat and white fumes, giving a strongly acid solution, from which potassium acetate and alcohol precipitate potassium perchlorate, identified by its optical properties under the microscope. These experiments show clearly that chlorine heptoxide is produced in quantity from illuminated chlorine dioxide. When traces of moisture are present, light, feathery crystals are produced which appear to be the monohydrate of perchloric acid, $HClO_4,H_2O$, m. p. 50°.

An approximate value for the percentage of chlorine dioxide changing to chlorine heptoxide was obtained by exposing the gas to sunlight until the colourless liquid was produced (4—7 hours' exposure). The pressure change was measured, using a narrow-bore mercury manometer with air buffer, which was only connected to the vessel through a tap for brief intervals, and the contents of the flask were washed out and titrated. No chlorine ion was found in the solution. The acidity was assumed to be due to chlorine heptoxide, and the iodine liberated on addition of potassium iodide was assumed to be due to chlorine. An average of numerous experiments showed that chlorine heptoxide formation was 65% by the titration, and 60% by the pressure measurement, of that required by the equation:

$$8ClO_2 \rightarrow 2Cl_2O_7 + 2Cl_2 + O_2.$$

The large formation of chlorine heptoxide is surprising in view of the difficulty of formulating a mechanism of the process. It is inconceivable on collisional probability grounds that the photochemical change is of a high reaction order, and the mechanism must therefore involve a series of consecutive reactions. A simple series cannot be found involving only the known oxides of chlorine. It was shown by comparison of two tubes exposed together, containing chlorine dioxide diluted with oxygen and with an equal volume of carbon dioxide, respectively, that the liquid formation occurred at the same rate in both. Molecular oxygen, therefore, does not appear to play a part in the sequence of changes. It will be seen later that possibly chlorine monoxide is produced, but this is not sufficient to account for the reaction. It is interesting in view of this that Hinshelwood and Prichard (J., 1923, **123**, 2730) found that the thermal decomposition of chlorine monoxide is a consecutive change involving unknown oxides of chlorine, and that Käbitz (*Diss.*, Bonn, 1905) found the same lines in the absorption spectra of chlorine monoxide and chlorine dioxide. It seems clear, then, that in the action of light and heat on chlorine monoxide and chlorine dioxide at least one unknown oxide of chlorine is produced which is very reactive.

In this connexion, the dark red substance colouring the liquid chlorine heptoxide in the initial stages of the photochemical decomposition of chlorine dioxide is of great importance. Unfortunately it was not found possible to obtain results of value by analysing it because of the presence of undecomposed chlorine dioxide and chlorine. Vorländer and Kaascht (*Ber.*, 1923, **56**, [*B*], 1162) found that chlorine dioxide dissolved in anhydrous perchloric acid gave a brownish-red substance. Our substance does not appear to be this, as we found that chlorine dioxide dissolved in a carbon tetrachloride solution of chlorine heptoxide, prepared by Meyer and Kessler's method (*Ber.*, 1921, **54**, 566), gave the characteristic bands of chlorine dioxide only, and did not show the continuous absorption in the blue and violet regions characteristic of the solutions obtained by dissolving the liquid, obtained photochemically, in carbon tetrachloride. On the other hand, the latter resembled the absorption band of chlorine monoxide solutions, and the likelihood that the red substance is chlorine monoxide is increased by the experiments on the thermal decomposition of chlorine dioxide. Dry gaseous chlorine dioxide, prepared in absolute darkness, and diluted with an equal volume of carbon dioxide, was found to remain without decomposition over periods of several hours at temperatures above 85°. When, however, the gas was exposed for a few seconds to an electric lamp, a great difference in the thermal stability was

observed. At 41°, decomposition, as observed with a manometer, took several hours; at 51·5°, it became explosive with a period of induction. At intermediate temperatures, autocatalytic curves with periods of induction were obtained, the reaction rate showing a remarkable sensitivity to temperature. These curious results were always obtained in many concordant repetitions, using different vessels. Additions of small quantities of chlorine or of oxygen were without effect, but moisture retarded the reaction.

Experiment then showed that a little chlorine monoxide added to unilluminated chlorine dioxide exactly reproduced the thermal decomposition curves obtained with the illuminated gas. Analysis of the residual gas showed that chlorine monoxide was still present. It thus seems not unlikely that chlorine monoxide is produced when light acts upon chlorine dioxide, but the explanation of this, and of the formation of the heptoxide, cannot be given by any simple hypothesis.

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OXFORD. [*Received, December 13th*, 1924.]

LXXII.—*The Nature of the Alternating Effect in Carbon Chains. Part I. The Directive Influence of the Nitroso-group in Aromatic Substitution.*

By CHRISTOPHER KELK INGOLD.

THE hypothesis, first advanced by Flürscheim,* that the introduction of a substituent may give rise to an effect which alternates through a whole chain of atoms has met with such success in the interpretation of organic chemical data † that at the present time no one doubts the existence in carbon chains of some property capable of alternating from atom to atom.

The theory has, however, been advanced in two distinct forms. According to Flürscheim's original hypothesis, it is the strength of chemical affinity which alternates. According to the hypothesis of alternating polarities, it is the electric charges (real or latent) on the atoms (Fry, Lapworth, Robinson and others). It happens that both these special interpretations frequently lead to identical pre-

* It is very difficult to trace the real beginnings of such ideas. Lapworth's «γ-rule may be regarded as a special case of the general proposition, and should be mentioned on account of its early date (1898).

† For applications to aromatic substitution, compare, for example, Flürscheim, *J. pr. Chem.*, 1902, [ii], **66**, 321; 1905, **71**, 497; 1907, **76**, 185; Fry, "The Electronic Conception of Valence," 1921; and for applications to strengths of acids and bases, Flürscheim, J., 1909, **95**, 718; 1910, **97**, 84.

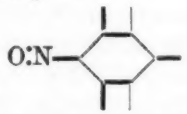
dictions, so that any new experimental illustration (and many have recently been given) of the existence of an alternating effect is not necessarily evidence in favour of either hypothesis. Crucial, and also simple, cases, in which the two hypotheses inevitably lead to opposite predictions, are not easily devised; but it is only by experiments on cases of this kind that an insight into the nature of the alternating effect can be gained.*

The conditions to be fulfilled in such an experiment may be seen from the postulates of the two theories. According to Flürscheim's hypothesis, the substituent atom giving rise to alternation—the "key-atom," to employ Lapworth's convenient name—acts by virtue of its disposable affinity. Tervalent nitrogen and bivalent oxygen both possess more unbound affinity than hydrogen, and, for instance, if attached to the benzene nucleus, will cause the development of free affinity in the *o*- and *p*-positions; that is, they will be *op*-directing. Their relative influence when competing will accord with their relative tendencies to attain a higher valency: tervalent nitrogen will have the greater influence. According to the polar view, on the other hand, it is the negative character of oxygen and nitrogen atoms which renders them *op*-directing, since a group directly entering in place of hydrogen must be positive. When competing, however, oxygen must predominate over nitrogen on account of the greater negativity of the former (*i.e.*, its more complete series of unrestrained electrons; Robinson, *Trans. Faraday Soc.*, 1923, **19**, 506; Kermack and Robinson, J., 1922, **121**, 427; Flürscheim, *Chem. and Ind.*, 1924, **43**, 1161). Again, on Flürscheim's hypothesis, effects of the opposite kind must be produced by a substituent atom having less disposable affinity than hydrogen, as, for instance, quinquevalent nitrogen; and the same prediction is achieved for the hypothesis of alternate polarities by treating as the key-atom, not the nitrogen atom itself, but *the more strongly negative oxygen atom* with which the quinquevalent nitrogen atom is usually combined. Thus it follows that the predictions of the two hypotheses are bound to agree as regards the directive effects of almost all the simpler groups.† In order to obtain the evidence sought, it is necessary to set counter to one another the postulated predominating effects of highly unsaturated tervalent nitrogen on

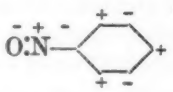
* The two hypotheses are not of necessity mutually exclusive. Thus Lapworth (*Chem. and Ind.*, 1924, **43**, 766) has admitted the necessity for Flürscheim's interpretation whilst claiming for the theory of alternate polarities an equal position as an additional factor. This possible superposition of alternating effects adds greatly to the difficulty of distinguishing between the two theories.

† Complex groups, especially those bound to the ring through carbon, require special consideration which it is proposed to defer to a later paper.

the one hand and highly electronegative oxygen on the other. The only simple groups fulfilling this condition are the nitroso- and hydroxylamino-groups, and of these the former alone is free from the complicating presence of hydrogen and other possible "key-atoms." The determination of the directive influence of the nitroso-group therefore possesses much greater importance than would normally attach to a similar case, because it is the simplest, indeed, perhaps, the only really simple, case which is crucial for either theory :—



(N = key atom; ∴ free affinity in *op*-positions; ∴ NO-group is *op*-directive.)



(O = key-atom; * ∴ *m*-carbon atoms negative; ∴ NO-group is *m*-directive.)

The facts, so far as they have been ascertained, are that nitrosobenzene can be directly chlorinated, brominated, and nitrated; and that in each case the group introduced enters mainly at the para-position; meta-isomerides could not be detected.†

Summary and Conclusions.—Whilst no inference of a general character can be drawn from these experiments, the results distinctly favour the view that directive effects in aromatic substitution are dependent on an alternation of quantity, rather than of electropolar quality, of chemical affinity.

Experimental.

(i) *Action of Bromine on Nitrosobenzene.*—A solution of pure nitrosobenzene (5 g.; freshly distilled in steam, crystallised, and dried) in dry carbon disulphide (50 c.c.) was treated as quickly as possible at −5° with a solution of bromine (7·5 g.) in the same solvent (75 c.c.). Most of the solvent and the dissolved hydrogen

* This allocation of signs can also be supported on experimental grounds, since the reactions of the nitroso-group closely resemble those of the carbonyl group, which is always written $-\overset{+}{C}=\overset{-}{O}$. The additions of Grignard reagents, and the condensations with malonic ester, and with amines, hydrazines, etc., may be cited as examples :—

$$C_6H_5\cdot\overset{+}{N}=\overset{-}{O} + \overset{-}{R}\cdot\overset{+}{Mg}\overset{-}{Br} \longrightarrow C_6H_5\cdot NR\cdot OMgBr.$$

$$C_6H_5\cdot\overset{+}{N}=\overset{-}{O} + \overset{+}{H_2}\overset{-}{C}(CO_2Et)_2 \longrightarrow C_6H_5\cdot N{:}C(CO_2Et)_2 + H_2O.$$

† These results are in agreement with, but simpler than, the indications that have previously been obtained; compare Bamberger, Büsdorf, and Sand (*Ber.*, 1898, **31**, 1513) on the polymerisation of nitrosobenzene, and Ingold and Weaver (J., 1924, **125**, 1456) on its ring additions with other unsaturated substances.

bromide were rapidly removed under diminished pressure, the concentrated solution was diluted with fresh ice-cold carbon disulphide, again reduced to a small volume, and the process repeated a third time. The liquid was then decanted from a small tarry deposit, allowed to evaporate in a current of air, and the crystalline residue distilled in steam, when the nitroso-compounds passed over (blue condensate) during the first 5—10 minutes.

p-*Bromonitrosobenzene.*—From the "nitroso-fraction," pure *p*-bromonitrosobenzene was readily separated by crystallisation from ethyl alcohol. It was identified by its m. p. (95°), by a mixed m. p.* with a specimen prepared by oxidation of *p*-bromoaniline, and by analysis (Found : C = 38·9; H = 2·2; N = 7·6; Br = 42·9. Calc., C = 38·7; H = 2·1; N = 7·5; Br = 43·0%). To make quite certain of its identity, it was condensed with a molecular proportion of aniline (warming for a few minutes in glacial acetic acid solution suffices), and the *p*-bromoazobenzene produced (m. p. 89°; orange leaflets from dilute acetic acid) identified with a specimen prepared in like manner from *p*-bromoaniline and nitrosobenzene. The yield of bromonitrosobenzene was variable, but amounted in some experiments to 40%. Part of the remaining material was accounted for as *pp'*-dibromoazoxybenzene, the normal auto-decomposition product of *p*-bromonitrosobenzene, part as *p*-bromonitrobenzene, its product of oxidation, and a further portion as unattacked nitrosobenzene. Doubtless, azoxybenzene and nitrobenzene also were present, but they were not isolated.

In order to search for possible isomerides the alcoholic mother-liquors from the *p*-bromonitrosobenzene from several experiments such as the above were combined, and evaporated at the ordinary temperature. The solid residue was warmed with an equal weight of aniline dissolved in excess of glacial acetic acid, and the resulting azo-compounds were isolated by dilution with water. Fractional crystallisation alternately from aqueous acetic acid and from ligroin gave a fairly sharp separation into *p*-bromoazobenzene and azobenzene (proof of the presence of unchanged nitrosobenzene in the "nitroso-fraction"), no third substance appearing to be present.

p-*Bromonitrobenzene.*—During the distillation in steam, a small quantity of solid continued to collect in the distillate for some hours after the whole of the nitroso-compounds had passed over. This

* Mixed m. p.'s are not of much value as evidence of identity amongst nitroso-compounds, since these substances have a marked tendency to form mixed crystals. Thus *p*-chloro- and *p*-bromo-nitrosobenzene melt at 93° and 95° respectively, and mixtures of the two melt between these limits. It was for this reason that the procedure of confirming all apparent identities through the corresponding azo-compounds was uniformly employed in these experiments.

product was collected, and crystallised from alcohol, when *p*-bromonitrobenzene, m. p. 125°, was obtained. It was identified by analysis (Found : C = 35·7 ; H = 2·1 ; Br = 39·5. Calc., C =35·6 ; H = 2·0 ; Br = 39·6%), and by a direct comparison with a genuine specimen.

pp'-*Dibromoazoxybenzene.*—The residue which did not distil in steam was crystallised (yellow plates) from benzene and identified as *pp'*-dibromoazoxybenzene by its m. p. (170—171°), and by a mixed m. p. and comparison with an authentic specimen.

(ii) *Action of Chlorine on Nitrosobenzene.*—This experiment was carried out like the last, and it proceeded in much the same way, except that a larger quantity of nitrosobenzene remained owing to loss of chlorine.

p-*Chloronitrosobenzene.*—After distillation in steam, this substance was separated from nitrosobenzene, and finally purified, by crystallisation from alcohol. Its identity was proved by its m. p. (92—93°), by analysis (Found : C = 50·9 ; H = 3·0. Calc., C = 50·9 ; H = 2·8%), by comparison with a specimen prepared by the oxidation of *p*-chloroaniline, and by its conversion, by condensation with aniline, into *p*-chloroazobenzene, orange-red prisms, m. p. 88°, a specimen of which was synthesised for comparison from *p*-chloroaniline and nitrosobenzene.

As in the previous experiment, the mother-liquors were searched, but, besides *p*-chloronitrosobenzene, only unchanged nitrosobenzene could be detected.

p-*Chloronitrobenzene and* pp'-*Dichloroazoxybenzene.*—The former, prisms, m. p. 83° (Found : C = 45·7 ; H = 2·5. Calc., C = 45·7 ; H = 2·5%), and the latter, needles, m. p. 155° (alone or mixed with a genuine specimen) were isolated, purified, and identified exactly like the corresponding bromo-compounds (above).

(iii) *Direct Nitration of Nitrosobenzene.*—This is a difficult operation on account of the tendency of the substance to oxidise to nitrobenzene, which, for example, is almost the sole product of the action of 100% nitric acid at 0°. However, experiments with mixtures of nitric acid and phosphorus pentoxide yielded definite evidence of the occurrence of nitration side by side with much oxidation. The best results were obtained by adding freshly-prepared crystalline nitrogen pentoxide to a solution of nitrosobenzene in carbon tetrachloride, containing some phosphorus pentoxide in suspension, and cooled in an efficient freezing mixture (ammonium nitrate). Even under these conditions a considerable amount of nitrobenzene was produced.

p-*Nitronitrosobenzene.*—The product was distilled in a current of steam, and the distillate collected by fractions during the first

½ hour. The oil extracted from each fraction by means of ether was mixed with ligroin after removing the ether, a process which caused the separation of crystals from certain of the later fractions. After crystallisation from alcohol (yellow needles), the substance was identified as *p*-nitronitrosobenzene by its m. p. (116°), by comparison with a specimen prepared from *p*-nitroaniline, and by conversion, by condensation with aniline, into *p*-nitroazobenzene (red leaflets, m. p. 134—135°), which was similarly identified by comparison with a specimen synthesised for the purpose.

The whole of the nitronitrosobenzene produced was not isolated in the free state, but the presence of a certain quantity remaining dissolved in the nitrobenzene was proved by boiling the mixture with an acetic acid solution of aniline, and removing the nitrobenzene in a current of steam after the addition of dilute sulphuric acid. The azo-compound (which appears to be somewhat volatile in steam, although much less so than nitrobenzene) was purified by crystallisation from acetic acid, and identified by direct comparison and by analysis (Found : C = 63·6; H = 4·2. Calc., C = 63·5; H = 4·0%).

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LXXIII.—*The Synthesis of Glycols from Atrolactinic Acid.*

By ROBERT ROGER.

THE Grignard reaction was employed in the course of work on asymmetric synthesis (McKenzie, J., 1904, **85**, 1249; 1906, **89**, 365; McKenzie and Wren, J., 1906, **89**, 688; McKenzie and Müller, J., 1909, **95**, 544), for example, in the asymmetric synthesis of atrolactinic acid :

$$\underset{\text{inactive}}{Ph\cdot CO\cdot CO_2H} \longrightarrow \underset{\text{active}}{Ph\cdot CO\cdot CO_2\cdot C_{10}H_{19}} \longrightarrow \underset{\text{active}}{OH\cdot CPhMe\cdot CO_2\cdot C_{10}H_{19}} \longrightarrow \underset{\text{active}}{OH\cdot CPhMe\cdot CO_2H}.$$

Here the experimental conditions were regulated so that the attack of magnesium methyl iodide on *l*-menthyl benzoylformate took place practically entirely at the carbonyl group to which the phenyl group is attached. A small amount of crude material also was isolated, and this, from its melting point, would seem to have been the pinacol, $OH\cdot CPhMe\cdot CMe_2\cdot OH$, but this side-issue was not further investigated at the time.

The syntheses of glycols of the type $OH{\cdot}CPhMe{\cdot}CR_2{\cdot}OH$ from ethyl atrolactinate by the Grignard reaction has now been investigated and several difficulties were found which were not altogether unexpected. By the action of magnesium methyl iodide on the ester under the usual conditions, only small amounts of the pinacol $OH{\cdot}CPhMe{\cdot}CMe_2{\cdot}OH$ were obtained, and with magnesium ethyl iodide the yield of the corresponding glycol was even smaller. By saponification of the resulting oils, a large proportion of the original atrolactinic acid was always recovered, indicating that the ester had been to a large extent unattacked, and that the small yield of glycol could not be attributed to its dehydration (Grignard, *Ann. Chim. Phys.*, 1901, [vii], **24**, 463; Slavjanov, *J. Russ. Phys. Chem. Soc.*, 1907, **39**, 140). When magnesium phenyl bromide was employed, however, action seemed to take place to a larger extent, but difficulty was also experienced at first in isolating the glycol from the viscous mass obtained. The use of anisole as the Grignard medium led to no improvement in the yield, just as Meerwein (*Annalen*, 1919, **419**, 121) had found in the action of magnesium ethyl iodide on ethyl diethylglycollate. Finally, I resorted to long periods of heating (11—25 hours) and this led to a marked improvement in the yields.

It would seem, therefore, that the carbethoxy-group in ethyl atrolactinate is very irresponsive to attack by the Grignard reagent, and for this reason the above-mentioned asymmetric syntheses were successful. An interesting light is thrown on the question by Bouvet (*Bull. Soc. chim.*, 1915, [iv], **17**, 202), who subjected ethyl oxalate to the action of various Grignard reagents. With magnesium methyl iodide the yields of pinacol were small, whilst with magnesium ethyl and benzyl halides the actions were restricted almost exclusively to the formation of the respective glycollic esters, $OH{\cdot}CEt_2{\cdot}CO_2Et$ and $OH{\cdot}C(CH_2Ph)_2{\cdot}CO_2Et$. With magnesium phenyl bromide, however, the yield of pinacol from ethyl oxalate was almost theoretical (Valeur, *Bull. Soc. chim.*, 1903, [iii], **29**, 683). Dilthey and Last (*Ber.*, 1904, **37**, 2639) also have investigated the latter reaction, and claim to have isolated β-benzpinacolin, but in proof of their claim they give neither analysis nor any chemical evidence for this compound. The action of magnesium ethyl bromide on ethyl oxalate has been the subject of further investigation by Meerwein (*loc. cit.*), who found that the action can progress a step further with the formation of the hydroxyketone, $OH{\cdot}CEt_2{\cdot}COEt$, but that this ketone will not react further with magnesium ethyl bromide to give the pinacol. He also obtained the same result starting from ethyl diethylglycollate. The selective action of the Grignard reagent can sometimes be explained by the

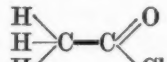
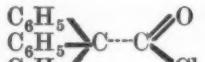
practical conditions employed (Hepworth, J., 1919, **115**, 1203), but the work of Meerwein on ethyl diethylglycollate would show that in certain examples there is a total inability of the carbethoxy-group to react completely. The same author also succeeded in isolating the hydroxy-ketones only in the action of magnesium propyl and butyl bromides on ethyl diethylglycollate. In contra-distinction to this, Meerwein (*loc. cit.*) and Parry (J., 1911, **99**, 1169; 1915, **107**, 108) have shown that esters of methylethyl- and dimethyl-glycollic acids react easily and completely with certain Grignard reagents.

The formation of pinacols from ethyl oxalate or from disubstituted glycollic esters is thus often a matter of considerable difficulty. The selective action of the Grignard reagent in the cases referred to may be accounted for in two ways. First, the two reactions : (*a*) ester $\longrightarrow$ hydroxy-ester, (*b*) hydroxy-ester $\longrightarrow$ pinacol, possess very different velocities, the second stage being the slower. Secondly, spatial effects lead to a complex which is not prone to attack by the reagent. The importance of spatial influences is well demonstrated in the preparation of *l*-benzoin from *l*-mandelamide and magnesium phenyl bromide (McKenzie and Wren, J., 1908, **93**, 312; 1910, **97**, 473). Here, in spite of the fact that a moderate excess of reagent was used, the ketol was isolated in fairly good yield. Moreover, it has since been found in this laboratory that the addition of a fresh Grignard reagent to the *l*-mandelamide-magnesium phenyl bromide complex does not lead to the formation of a substituted hydrobenzoin unless the *l*-benzoin is actually isolated.

This reluctance of the carbethoxy-group to react with the Grignard reagent in the cases mentioned naturally suggests that some form of steric hindrance had been brought into play. This is supported by the fact that malonic, succinic, and adipic esters react readily under similar conditions to those employed for ethyl oxalate, but good yields of pinacol are obtained (Valeur, *Compt. rend.*, 1901, **132**, 834; Bouvet, *loc. cit.*; Zelinsky and Kravetz, *J. Russ. Phys. Chem. Soc.*, 1906, **38**, 931; Slavjanov, *loc. cit.*). Moreover, when disubstituted malonic esters are employed, the reaction is restricted more or less to one carbalkyloxy-group, the controlling factors being, according to Kalischev (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 427), both the nature of the substituent and the Grignard reagent groups.

The work carried out by Meerwein and by Tiffeneau on pinacolinic and semipinacolinic transformations renders those results less anomalous. These authors classify the various alkyl and aryl groups in order of their saturation capacities. Thus, ethyl and benzyl have a low, methyl and *iso*butyl a moderate, whilst phenyl and other

aromatic groups have a large saturation capacity. That such a conception can play a *rôle* in other directions is demonstrated by, for example, the work of Auwers and Schaich on the alkylation of indazole (*Ber.*, 1921, **54**, 1738) and of Auwers and Wegener on the opening of the ring in substituted coumarones (*J. pr. Chem.*, 1923, [ii], **106**, 226). Similarly, the effect of substitution on the reactivity of the carboxyl group is pronounced when the properties of acetic and triphenylacetic acids are contrasted. Gomberg has shown that the saturating effect of three phenyl groups attached to a single carbon atom is such that tervalent carbon is a practical possibility, and thus in triphenylacetic acid the carboxyl group is rendered very stable. Triphenylacetyl chloride does not therefore react with water readily, owing to the large valency power free to hold the chlorine atom to the carbon :

Compare  and  [Schmidlin and Hodgson (*Ber.*, 1908, **41**, 438)].

Doubtless there will be a variation in the reactivity of the carboxyl groups in the different substituted glycollic acids. Thus, ethyl diethylglycollate will react only partially with a group of small saturation capacity, such as ethyl, giving the hydroxy-ketone. The enfeebling effect of the low capacity of the ethyl group is well marked in Grignard's work on ethyl ethylacetoacetate and ethyl diethylacetoacetate. The former of those compounds, on heating at 100° with magnesium methyl iodide, gave the glycol along with some unchanged ester, but with the latter more than one-half of the ester was recovered unattacked and no trace of the glycol was found. Salkowski (*J. pr. Chem.*, 1923, [ii], **106**, 253) explains this by the formation of an oxonium compound, $O{=}C{<}{+}MgCH_3I \rightarrow >C{=}O{<}^{CH_3}_{MgI}$. This reverts readily in the latter case to the original compound, as " sicherlich der Grund liegt in der geringeren Additions-fähigkeit der Carbonyl Gruppe." Ethyl dimethylacetoacetate, however, gives fairly good yields of the glycol (Slavjanov, *loc. cit.*). Ethyl methylethylglycollate and methyl hydroxytrimethylbutyrate react fairly readily with magnesium methyl iodide, but the former reacts better with magnesium phenyl bromide. An ester such as ethyl dimethylglycollate, containing two groups of moderate capacity, reacts with most reagents. Ethyl benzilate reacts very readily with either phenyl or methyl reagents (Acree, *Ber.*, 1904, **37**, 2753; Erdmann, *Inaug. Diss.*, Rostock, 1910).

Ethyl atrolactinate would fall between the two extremes. When

the ester was heated for 3—4 hours with magnesium methyl iodide, a poor yield of pinacol was obtained. The same result was arrived at, starting from ethyl benzoylformate. When magnesium ethyl bromide was employed under similar conditions, the yield was very much smaller, most of the ester being recovered unattacked. On extending the heating period to 20—25 hours, however, a 65% yield of pinacol was obtained. With magnesium phenyl bromide, a good yield of glycol was obtained by heating for 9 hours. The latter glycol was also synthesised by the action of magnesium phenyl bromide on methylbenzoin, OH·CPhMe·COPh, and by the action of magnesium methyl iodide on phenylbenzoin, OH·CPh_2·COPh, good yields being obtained in both cases.

Experimental.

β-Phenyl-γ-methylbutylene βγ-Glycol, OH·CPhMe·CMe_2·OH.—The Grignard solution, prepared from methyl iodide (43 g.), was added to an ethereal solution of ethyl atrolactinate (10 g.), the mixture being agitated mechanically. No very vigorous action took place, and the mixture was boiled (4 hours) before decomposition with ice and dilute sulphuric acid. On crystallising the resulting oil from light petroleum, 3·5 g. of solid were obtained (yield 37%). The pure substance, obtained after several crystallisations from light petroleum, crystallised from light petroleum in rosettes of slender needles, m. p. 83·5—84·5° (Found : C = 73·4; H = 8·9. Calc., C = 73·3; H = 9·0%). Lepin (*J. Russ. Phys. Chem. Soc.*, 1912, **44**, 1165), who prepared the glycol by hydration of the corresponding oxide, gives the m. p. 83—84°. A trace of the glycol gives a faint yellowish-green coloration which assumes a pink tint on standing for some time with concentrated sulphuric acid. The oil obtained from the mother-liquors from the crystallisations gave two products on hydrolysis with caustic potash. (1) By extraction of the alkaline liquors an oil, which did not crystallise, was obtained. (2) By extraction of the acidified liquors, atrolactinic acid (2·1 g.), m. p. 88—90°, was obtained.

The same glycol was also synthesised by the action of magnesium methyl iodide on ethyl benzoylformate as described above. The yield was poor, and was not improved by the use of anisole as the Grignard medium.

αα β-Triphenylpropylene αβ-Glycol, OH·CPhMe·CPh_2·OH.—Various unsuccessful attempts were made to obtain this glycol from magnesium phenyl bromide and ethyl atrolactinate in the manner described above. It was eventually obtained as follows : Ethyl atrolactinate (20 g.) was added to a solution of magnesium phenyl bromide, prepared from bromobenzene (80 g.), and the mixture was then

boiled for 11 hours. After decomposing with ice and ammonium chloride, an oil was obtained from which 15 g. of crude solid were separated by dissolving in benzene and light petroleum. The pure glycol, m. p. 76—77°, was obtained after several crystallisations from benzene–light petroleum (Found: C = 83·1; H = 6·8. Calc., C = 82·9; H = 6·6%). With concentrated sulphuric acid, it gives a yellow coloration deepening to an emerald-green.

This pinacol was also synthesised: (1) By the action of magnesium methyl iodide (6 mols.) on phenylbenzoin (1 mol.), prepared from benzil and magnesium phenyl bromide. (2) *Methylbenzoin*, OH·CPhMe·COPh, prepared from magnesium methyl iodide and benzil, crystallises from light petroleum in rosettes of clear needles, m. p. 65—66° (Found: C = 79·3; H = 6·35. Calc., C = 79·6; H = 6·23%). Methylbenzoin (10 g.; 1 mol.) was added to the ethereal solution of magnesium phenyl bromide (4 mols.). The mixture was boiled for 12 hours, and was then decomposed with ice and ammonium chloride. The pinacol was separated and recrystallised as before (yield 6 g.). Both specimens melted at 76—77°, alone or mixed with the pinacol obtained from ethyl atrolactinate.

β-*Phenyl*-γ-*ethylamylene* βγ-*Glycol*, OH·CPhMe·CEt_2·OH.—The employment of the same conditions for the preparation of this compound as for the action of magnesium methyl iodide on ethyl atrolactinate gave only meagre yields of the glycol. Another attempt was made by allowing the reaction mixture to remain at the ordinary temperature for 14 days, but the ester seemed to be almost completely unattacked. The use of anisole as the Grignard medium was also unsuccessful. Ultimately, the ester (10 g.; 1 mol.) was heated with magnesium ethyl bromide (12 mols.) for 21 hours, and then decomposed with ice and dilute sulphuric acid. From the ethereal layer, 7 g. of the crude solid were separated. The pure pinacol was obtained by crystallising from light petroleum. Yield 6 g. (Found: C = 75·0; H = 9·9. Calc., C = 75·0; H = 9·7%).

The glycol crystallises from light petroleum in slender, pointed needles, m. p. 70—71°. It gives a faint yellow-green coloration with concentrated sulphuric acid, and when added to sulphuric acid (*d* 1·55) it liquefies and develops a marked camphoraceous odour.

The author wishes to express his thanks to Professor McKenzie, F.R.S., for supervising this work, also to the Department of Scientific and Industrial Research and to the Carnegie Trust for their financial assistance.

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LXXIV.—*The Preparation of Pure Methyl Alcohol.*

By HAROLD HARTLEY and HUMPHREY RIVAZ RAIKES.

FOR the purposes of a general investigation of the properties of methyl alcohol as a solvent which is in progress in this laboratory, it was necessary to devise a method by which pure methyl alcohol could be prepared rapidly. The following communication is based on the work of Messrs. A. T. L. Allen, F. K. Ewart, J. E. Frazer, G. Nonhebel, and W. F. K. Wynne-Jones.

In addition to water, the chief impurities which may be present in the commercial alcohol are acetone and formaldehyde: these must be removed before it is dried. Acetone may be estimated either by the sodium hypoiodite method of Bates, Mullaly, and Hartley (J., 1923, **123**, 401), or in the following way, suggested by Mr. J. E. Marsh, F.R.S., which is better adapted to the estimation of very small quantities. Two c.c. of a concentrated stock solution of mercuric cyanide in 6*N*-sodium hydroxide are added to 2 c.c. of alcohol, and the mixture is warmed to boiling. A white precipitate indicates the presence of a ketone; if the precipitate darkens on standing, the presence of an aldehyde or of a mixture of aldehyde and ketone is inferred. These precipitates settle rapidly, and their bulk may be compared with those produced by alcohol containing known amounts of aldehyde or acetone. When the impurities are present singly, 0·002% of acetone or 0·004% of formaldehyde can be detected, though at the limit it is difficult to differentiate between the two (W. F. K. W.-J.). When the acetone content was greater than 0·02%, it was removed by the method described by Bates (*loc. cit.*).

Removal of Water.—The usual method of drying alcohol by refluxing over freshly burnt lime for several days (Danner, *J. Amer. Chem. Soc.*, 1922, **44**, 2834; McKelvy, *Bull. Bur. Standards*, 1913, **9**, 327) proved to be slow and wasteful, since about 20% of the alcohol was retained by the lime after distillation from a water-bath. Metallic calcium also is unsatisfactory, as it introduces volatile impurities, such as ammonia, which are difficult to remove. Sodium is an inefficient drying agent owing to the equilibrium $NaO{\cdot}CH_3 + H_2O \rightleftharpoons NaOH + CH_3{\cdot}OH$, an objection which applies also, though in a lesser degree, to the use of baryta or lime (compare Crismer, *Chem. Zentr.*, 1904, **1**, 1749; W. A. Noyes, *J. Amer. Chem. Soc.*, 1923, **45**, 857).

It was finally decided to use simple fractionation as the principal means of dehydration (S. Young, *Sci. Proc. Roy. Dublin Soc.*, 1910, **12**, 374), followed by distillation from aluminium methoxide

(McKelvy, *loc. cit.*, p. 364). For the fractionation, Hempel * columns with an effective length of 1·3 metres were connected to the distilling flasks by mercury seals, and mercury cups were also provided at the still-heads for the thermometer, contact between hot alcohol vapour and cork being thereby avoided. Soda-lime tubes were attached to the receiver, and all corks were covered with tin-foil. After its boiling point had become constant to 0·05°, the alcohol was fractionated once more and then refluxed under a column with aluminium amalgam (3 g. per litre) until all the aluminium had reacted, when it was distilled as before. The amalgam was made by warming pieces of thin sheet aluminium with a solution of mercuric chloride in dry alcohol. In all cases distillation was carried out at the rate of two drops a second, the first 50 c.c. and the last quarter of the distillate being rejected. Under these conditions, no difficulty arose from the volatility of aluminium methoxide (compare Walden, Ulich, and Laun, *Z. physikal. Chem.*, 1924, **111**, 275). Magnesium (Bjerrum and Zechmeister, *Ber.*, 1923, **56**, [*B*], 894) was found less satisfactory than aluminium.

For electrochemical work it was necessary to free the alcohol from ammonia and similar volatile impurities. This was accomplished by refluxing it for 6 hours with freshly dehydrated copper sulphate (2 g. per litre) under a short column up which a current of pure dry air was passing. It was then distilled rapidly through this column, condensed in block tin, and run through a conductivity cell of the siphon type into a collecting flask of hard glass. The specific conductivity of any portion of the distillate could thus be determined without risk of contamination. By carrying out the distillation at a very rapid rate, and by rejecting the first runnings, alcohol of specific conductivity 0·04 reciprocal megohms was readily obtained: it was preserved in Jena glass flasks having an "outside ground" cap. Sulphanilic acid (Goldschmidt, *Z. physikal. Chem.*, 1912, **81**, 30) was found less efficient than copper sulphate.

Distillation of the dry conductivity alcohol from silver nitrate in order to free it from reducing agents (Pearce and Mortimer, *J. Amer. Chem. Soc.*, 1918, **40**, 509; Partington, *Trans. Faraday Soc.*, 1923, **18**, 414), a procedure which may introduce other impurities, was found to be unnecessary, no aldehyde being detected by the mercuric cyanide test, and solutions of silver nitrate remaining colourless indefinitely. The distillation from aluminium would remove any oxidation products which might have accumulated during earlier fractionations.

* Dufton's copper spiral type is inapplicable owing to the danger of catalytic oxidation.

Detection and Estimation of Water.—The detection and estimation of small traces of water in methyl alcohol are matters of considerable difficulty. Anhydrous copper sulphate is useless for the purpose, as it forms a slightly soluble, bluish-green compound, stated to be $CuSO_4$,2MeOH (L. de Bruyn, *Rec. trav. chim.*, 1893, **11**, 112).

For the rapid estimation of the water content with an accuracy of 0·02%, the cuprous acetylide test described by Weaver (*J. Amer. Chem. Soc.*, 1914, **36**, 2462) was found convenient. This is based on the reaction of any water with calcium carbide to form acetylene, which remains dissolved in the alcohol and can be detected with an ammoniacal cuprous chloride solution. The latter is conveniently made fresh for each batch of tests by mixing equal volumes of the following solutions (Solution A : 3 g. of cupric chloride, 6 g. of ammonium chloride, and 9 c.c. of 0·88 ammonia in 100 c.c. of water. Solution B : 12 g. of hydroxylamine hydrochloride in 100 c.c. of water).

Quantitative results could be obtained as follows (G. N.). Two small pieces of carbide are covered with 3 c.c. of dry alcohol. After boiling gently for a minute to remove acetylene from the interstices of the carbide, the liquid is filtered. On addition of the cuprous solution, only a trace of colour should be developed; this serves as a blank test. Meanwhile another 2 c.c. of alcohol are added to the prepared carbide, the tube corked and left for one minute, with occasional shaking. The liquid is then filtered into 1 c.c. of the testing solution. The pink colour which develops is compared with standards of methyl-red. The trustworthiness of the test was confirmed by a series of viscosity measurements (J. E. F.), but being of an empirical nature it is necessary to observe the same procedure in every case. Commercial carbide, which is treated with paraffin during manufacture, is not sufficiently active for this test.

Accurate density determinations admit of the estimation of water to at least 0·01%, but are somewhat lengthy for routine work. We have found (F. K. E.) $d_{4^\circ}^{25^\circ} = 0{\cdot}78641$ as a mean of four concordant determinations, using two pyknometers and different samples of alcohol. This value is slightly lower than that interpolated from data in the literature.

Relative viscosity determinations in an Ostwald viscosimeter allow of the estimation of water with a limit of 0·025%, as the presence of 0·1% of water increases the time of flow by 0·4%, and with a suitable viscosimeter the time of flow can be determined with an accuracy of one part in a thousand. The absolute viscosity

of alcohol which had been subjected to fractionation alone and to treatment with aluminium also was found to be 0·00545 at 25° (F. K. E.), the viscosity of water at that temperature being taken as 0·00895 (Bingham and White, J., 1913, **103**, 959). Dunstan and Thole (J., 1914, **105**, 782) found 0·00546.

The most sensitive test for water is the determination of the electrical conductivity of a dilute solution of hydrogen chloride in the alcohol, provided that the absence of ammonia has been proved by determining the conductivity of the pure solvent. Goldschmidt (*Z. physikal. Chem.*, 1924, **108**, 121) has shown that $\Lambda^{25°}$ at 0·001*N* is depressed from 181·8 to 178·3 by the presence of 0·025% of water. We have found values of 181·5 and 181·0, indicating that the amount of water in the alcohol was less than 0·01%.

In conclusion, we wish to express our thanks to the Chemical Society for grants which defrayed part of the cost of the work.

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[*Received, October* 31*st*, 1924.]

LXXV.—*Studies of Equilibrium in Systems of the Type* $Al_2(SO_4)_3$–M''SO_4–H_2O. *Part I. Aluminium Sulphate–Copper Sulphate–Water and Aluminium Sulphate–Manganous Sulphate–Water at* 30°.

By ROBERT MARTIN CAVEN and THOMAS CORLETT MITCHELL.

THE present investigation is part of an attempt to discover a connexion between double-salt formation and differences of electropositiveness between the kations of component salts. At the same time it is hoped to throw light on the question of the existence of " pseudo-alums."

The previous literature on the subject is for the most part descriptive. Thus, Klauer (*Annalen*, 1835, **14**, 261) described the preparation of ferrous and magnesium pseudo-alums in presence of excess of sulphuric acid. Rammelsberg (*Pogg. Ann.*, 1838, **43**, 399) dealt with various naturally occurring double salts containing aluminium sulphate. Kane (*ibid.*, 1838, **44**, 472) mentioned $MnSO_4,Al_2(SO_4)_3,22H_2O$, apjohnite, a naturally occurring salt found and described by Apjohn (*Proc. Roy. Irish Acad.*, 1839, **1**, 51),

and Wirth (*Z. angew. Chem.*, 1913, **26**, 81) discussed the system aluminium sulphate–ferrous sulphate–water.

Experimental.

The equilibrium mixtures in the case of the copper sulphate system were obtained as follows: Pure recrystallised copper sulphate and aluminium sulphate were placed with water in separate flasks in a thermostat at 40°. A large vessel, fitted with a cork carrying a stirrer and filtering device, was kept in another thermostat at 30° ± 0·1°, and in this were placed mixtures in different proportions of the two single salt solutions.

The mixtures were stirred for 3 days, and each resulting solution was then decanted through a filter into a weighing-bottle, both kept at the temperature of the bath. The solid phase also was rapidly drained by suction and transferred while moist to a weighing-bottle. The solution and moist solid phase were then weighed, and made into solutions measuring known volumes.

The copper was estimated iodometrically, and the aluminium was calculated after determination of the total sulphate.

The system $MnSO_4$–H_2O shows a transition point at 26°, whereafter the solubility decreases. It was therefore of no advantage to commence with a solution of manganous sulphate above this temperature. In this case solutions of the single salts, saturated at room temperature, were mixed in the reaction vessel and isothermally evaporated by means of a filtered current of air, with constant stirring. When a solid phase separated, the current of air was stopped, and stirring continued for 3 days, whereafter the solution and solid phases were removed for analysis.

Manganese was estimated by precipitating it as hydrated dioxide [using ammonium persulphate in presence of excess of sulphuric acid as recommended by Knorre (*Z. angew. Chem.*, 1901, **14**, 1149)], dissolving the precipitate in standard oxalic acid, and titrating the solution with permanganate. Aluminium was again calculated after the determination of total sulphate.

It has been noted (Britton, J., 1922, **121**, 982) that aluminium sulphate hydrolyses above 30°. In the experiments carried out, the amount of hydrolysis in the single solutions from which equilibrium systems were obtained was, however, exceedingly small and was neglected.

All the solutions were extremely viscous, especially in the manganous sulphate system, and considerable difficulty was experienced in handling them. Each result, however, was duplicated.

Results.

The quantities in the tables are expressed as g. per 100 g. of solution (for the solutions) or of moist solid (for the rests).

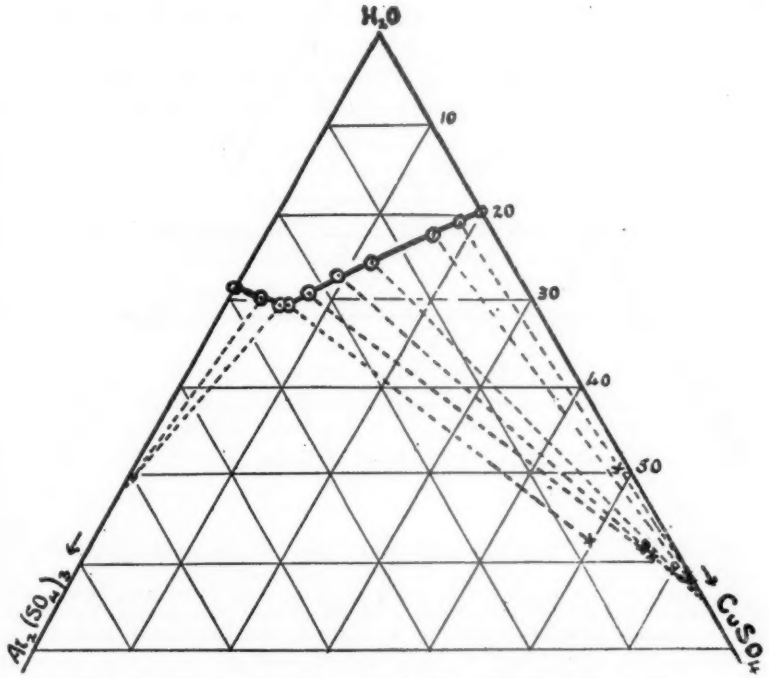


FIG. 1.—*Equilibrium Diagram* $Al_2(SO_4)_3$–$CuSO_4$–H_2O *at* 30°.

That no combination occurs between aluminium sulphate and cupric sulphate is shown by the absence of a double-salt curve, and by the fact that broken lines drawn through "solution" points and appropriate "rests" intersect at points corresponding with the composition of the single salts.

$Al_2(SO_4)_3$–$CuSO_4$–H_2O (see Fig. 1).

Solutions.			Rests.		
$Al_2(SO_4)_3$.	$CuSO_4$.	H_2O.	$Al_2(SO_4)_3$.	$CuSO_4$.	H_2O.
nil.	20·33	79·67	—	—	—
2·75	18·65	78·60	0·92	48·61	50·47
5·97	16·76	77·27	0·13	61·72	38·15
13·80	12·13	74·07	1·51	59·38	39·11
17·65	9·79	72·56	3·21	55·25	41·54
22·00	7·67	70·33	2·94	56·69	39·37
24·64	6·30	69·06	8·20	49·78	42·02
25·22	5·74	69·04	50·1	0·30	49·60
26·83	3·39	69·78	49·52	0·25	50·23
28·86	nil.	71·14	—	—	—

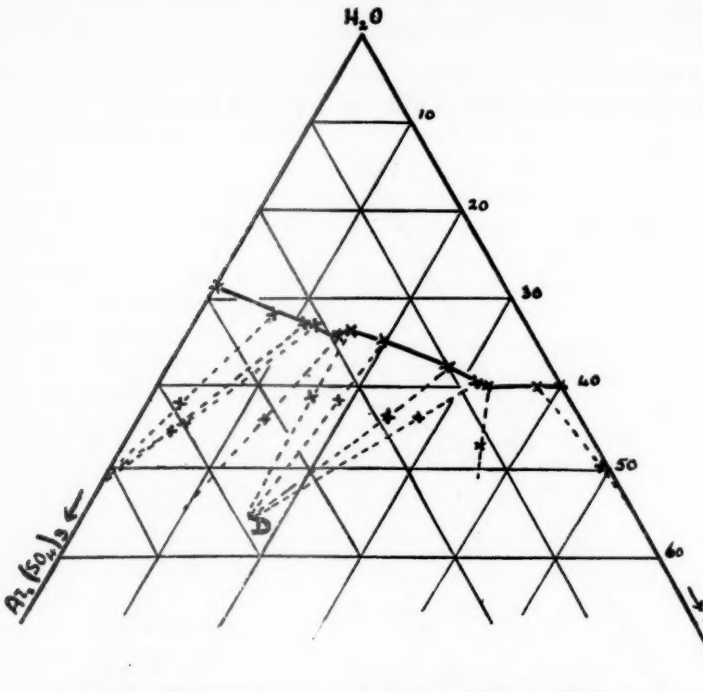


FIG. 2.—*Equilibrium Diagram* $Al_2(SO_4)_3$–$MnSO_4$–H_2O *at* 30°.

The existence of a double salt is indicated by the curve intervening between the aluminium sulphate and manganous sulphate curves. The composition of this salt is shown, by the co-ordinates of the point D, at which broken lines drawn through "rests" intersect, to be $Al_2(SO_4)_3,MnSO_4,22H_2O$.

$Al_2(SO_4)_3$–$MnSO_4$–H_2O (see Fig. 2).

Solutions.			Rests.		
$Al_2(SO_4)_3$.	$MnSO_4$.	H_2O.	$Al_2(SO_4)_3$.	$MnSO_4$.	H_2O.
nil	40·03	59·97	—	—	—
2·47	37·94	59·59	1·12	49·03	49·85
7·21	32·97	59·82	11·71	35·23	53·06
8·43	31·43	60·14	16·29	27·76	55·95
10·40	27·39	62·21	18·82	24·62	56·56
15·01	19·91	65·08	22·75	19·11	58·14
18·11	15·96	65·93	25·27	16·15	58·58
19·58	15·23	65·19	31·43	12·21	56·36
21·13	12·14	66·73	39·90	4·95	55·15
21·93	11·09	66·98	41·65	4·72	53·63
24·42	7·41	68·17	38·96	3·12	57·92
28·86	nil.	71·14	—	—	—

Conclusion.—It is evident, in the case of the cupric sulphate system, that no double salt is formed at 30°.

In the manganous sulphate system the compound

$$Al_2(SO_4)_3,MnSO_4,22H_2O$$

is formed.

This salt, which occurred as the solid phase, but was not separated from adhering solution, was seen to consist, as mentioned by Apjohn, of fine, needle-shaped crystals, with a peculiar property of knotting up into masses not unlike tapioca.

It is submitted that the term "pseudo-alum" should not be applied to this salt, which shows no resemblance to the alums.

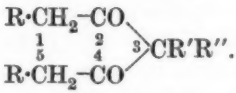
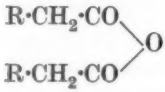
The authors desire to express their thanks to the Department of Scientific and Industrial Research for a grant and also to the Governors of the Royal Technical College for aid which has enabled one of them (T. C. M.) to participate in this research.

THE ROYAL TECHNICAL COLLEGE,
GLASGOW. [*Received, December* 19*th*, 1924.]

LXXVI.—*Interactions of Tellurium Tetrachloride and Acetic Anhydride.*

By GILBERT T. MORGAN and HARRY DUGALD KEITH DREW.

DURING the last three years it has been demonstrated by a comprehensive series of experiments that tellurium tetrachloride condenses to form cyclic compounds with β-diketones (I) in their diketonic form, and accordingly the diketone may contain two alkyl substituents on the carbon atom 3 so long as the terminal carbon atoms 1 and 5 are present as methylene groups.

(I.)  (II.) 

(R, R′, R″ are hydrogen atoms, or alkyl or arylalkyl groups.)

So far as these researches have been carried, it has been found that any diketone of general formula I furnishes a chelate group to tellurium and gives a *cyclo*telluripentanedione dichloride (III) which can be reduced quantitatively to the corresponding *cyclo*-telluropentanedione (IV).

(III.) (IV.)

Since the foregoing processes may be regarded as general reactions, the 3-methylene group or its homologue plays no direct part in the condensation, and it appeared likely that this group

might be replaced by oxygen as in the aliphatic anhydrides (II). The experiment has been tried on acetic anhydride with the following results.

With tellurium tetrachloride and a large excess of acetic anhydride (6 mols.) in chloroform, condensation takes place and hydrogen chloride is evolved. The chief product is *dichlorotelluridiacetic acid* (V), a colourless, crystalline substance stable in moist air, m. p. 160—161° (yield 50% on $TeCl_4$), the production of which is probably consequent on the formation of a sensitive cyclic anhydride,

$$Cl_2Te\begin{<}CH_2\cdot CO\\CH_2\cdot CO\end{>}O.$$

Reduction with alkali metabisulphite converts the dichloro-compound (V) quantitatively into *tellurodiacetic acid* (VI), a dichroic substance (pale yellow and colourless forms) exhibiting also dimorphism, m. p. 140—141°.

$$Cl_2Te\begin{<}CH_2\cdot CO_2H\\CH_2\cdot CO_2H\end{} \rightarrow Te\begin{<}CH_2\cdot CO_2H\\CH_2\cdot CO_2H\end{} \qquad \begin{matrix}Te\cdot CH_2\cdot CO_2H\\ \|\|\\Te\cdot CH_2\cdot CO_2H\end{matrix}$$

(V.) (VI.) (VII.)

The discovery of the preceding telluro-compound (VI) completes the series $O(CH_2\cdot CO_2H)_2$, $S(CH_2\cdot CO_2H)_2$, and $Se(CH_2\cdot CO_2H)_2$.

When exposed to moist air, tellurodiacetic acid is slowly oxidised in solution to amorphous oxytelluridiacetic acid. It is regenerated from this product by the action of bisulphite. Tellurodiacetic acid forms soluble yellow ammonium and sodium salts, whereas the white silver salt is amorphous and insoluble.

With $1\frac{3}{4}$ to 2 molecular proportions of acetic anhydride the condensation takes a different course and a grey flocculent solid separates from the concentrated chloroform solution. This deliquescent product, which consists probably of a mixture of trichlorotelluri-derivatives, $TeCl_3\cdot CH_2\cdot CO_2H$ and $(TeCl_3\cdot CH_2\cdot CO)_2O$, is reduced to *ditellurodiacetic acid* (VII), which separates in large, orange-red to ruby-red prisms, m. p. 144°, moderately soluble in water to a yellow solution.

The new acid forms soluble alkali salts and an orange silver salt which is photosensitive. From the final mother-liquors of this condensation separate colourless crystals of *methylene bistelluritrichloride*, m. p. 173° (VIII).

$$CH_2\begin{<}TeCl_3\\TeCl_3\end{} \rightarrow CH_2\begin{<}Te\\Te\end{} \qquad CH_2\begin{<}TeCl_2\cdot CH_2\cdot CO\cdot CH_3\\TeCl_2\cdot CH_2\cdot CO\cdot CH_3\end{}$$

(VIII.) (IX.) (X.)

This substance, which no longer contains oxygen, is sensitive to moist air, becoming hydrolysed to oxychloride. It condenses

with acetone and other ketones to give well-defined, crystalline compounds such as *methylenebistelluriacetone dichloride* (X).

When reduced with bisulphite, methylenebistelluritrichloride loses all its chlorine and becomes converted into *ditelluromethane* (IX), a dark brownish-red, insoluble product changing slowly into a black powder, this alteration occurring rapidly at 40°; it explodes on heating more strongly. Ditelluromethane cannot be vaporised without decomposition and moreover it is insoluble in all the usual solvents. Hence its molecular complexity has not been ascertained. Probably both red and black varieties are polymerides, $(CH_2Te_2)_x$.* They react, however, towards chlorine or bromine to regenerate substances of the type $CH_2(TeX_3)_2$, where X is the halogen atom.

The acetic anhydride condensation has furnished other telluriferous by-products which together with the foregoing derivatives are still under examination.

The formation of a methylene compound (VIII) during these condensations is of considerable theoretical interest, since the production of the $-CH_2-$ group from acetic anhydride must involve a profound disruptive change, which would scarcely be anticipated in view of the mild conditions employed in the interactions. Methylenebistelluritrichloride may arise in one of the following ways :—

1. Scission of carbon dioxide and hydrogen chloride from trichlorotelluriacetic acid and tellurium tetrachloride :—

$$Cl_3Te{\cdot}CH_2{\cdot}CO_2H + TeCl_4 = CH_2(TeCl_3)_2 + CO_2 + HCl.$$

But for this decomposition there is little precedent.

2. Elimination of water and carbon suboxide from acetanhydrobistelluritrichloride :—

$$(Cl_3Te{\cdot}CH_2{\cdot}CO)_2O \longrightarrow (Cl_3Te)_2CH_2 + H_2O + C_3O_2.$$

The brownish-red solutions from which methylenebistelluritrichloride is obtained suggest the presence of substances derived from carbon suboxide.

3. Intermediate formation of keten :—

$$CH_2{:}CO + 2TeCl_4 \longrightarrow CH_2(TeCl_3)_2 + COCl_2.$$

The reactions suggested under headings 2 and 3 require a dehydrating agent and tellurium tetrachloride would probably function in this way.

Attention should be directed to the development of colour among unsaturated tellurium derivatives. Tellurodiacetic acid, containing

* The cyclic structure $CH_2\langle\begin{matrix}Te{\cdot}Te\\Te{\cdot}Te\end{matrix}\rangle CH_2$ for ditelluromethane accords with the above suggestion of polymerism, but so far there is no experimental evidence for or against a twofold complexity.

only one atom of tellurium, is colourless or yellow, *cyclo*telluropentanediones are yellow, whereas compounds having a junction of two tellurium atoms in their molecules are more intensely coloured, ditellurodiacetic acid is red, and ditelluromethane is red or black. These colour differences offer a useful guide to the chemical constitution of organotellurium compounds.

Experimental.

Dichlorotelluridiacetic acid (V).—The turbid yellow solution of 20 g. of tellurium tetrachloride, 48 g. of acetic anhydride, and 150 c.c. of dry chloroform, when heated under reflux, rapidly evolved hydrogen chloride, and, after 4 hours, the liquid, decanted from elemental tellurium, was diluted with chloroform and the clear reddish-brown solution concentrated until a flocculent precipitate of grey crystals separated. Several crops of this product were collected, amounting in all to 13 g. The freshly separated material was deliquescent, but when kept in a vacuum desiccator, which was occasionally open, the substance became stable to moist air and the melting point rose to about 159°. This compound dissolved in cold acetone diluted with chloroform and was obtained crystalline by fractional precipitation with petroleum (b. p. 40—60°). Further purification was effected by adding petroleum to its solution in ethyl acetate and chloroform, when the compound separated in transparent, colourless, compact prisms, m. p. with intumescence 160—161°: 0·1743 gave 0·0952 CO_2 and 0·0317 H_2O, C = 14·90, H = 2·04; 0·1936 and 0·1104 gave 0·1752 and 0·0996 AgCl, Cl = 22·39, 22·32; 0·2485 gave 0·1004 Te, Te = 40·40. $C_4H_6O_4Cl_2Te$ requires C = 15·17, H = 1·91, Cl = 22·41, Te = 40·29%.

The dichloride separated from ethyl acetate–chloroform–petroleum either with or without ethyl acetate of crystallisation depending on the proportion of this solvent in the medium. The crystals containing solvent separated as spear-shaped needles or as vitreous, acicular prisms. These forms when powdered commenced to melt below 100° and gradually lost solvent in the desiccator.

The dichloride was insoluble in petroleum or benzene, very slightly soluble in chloroform, but dissolved readily in ether, acetone, alcohol, or acetic anhydride; in hot water it passed into solution, but with hydrolysis.

The oily mother-liquor from the foregoing preparation yielded small quantities of (1) *methylenebistelluritrichloride*, (2) a substance, not yet identified, forming colourless masses of woolly needles from acetone–benzene–petroleum, which intumesced at 152—153° and on reduction with aqueous metabisulphite yielded a red insoluble telluriferous product.

Tellurodiacetic Acid (VI).—When reduced with aqueous potassium metabisulphite (2·8 g. in 25 c.c.), dichlorotelluridiacetic acid (2 g.) gave with evolution of sulphur dioxide a pale yellow solution containing a suspension of grey needles. Repeated extraction of this product with small quantities of ether furnished tellurodiacetic acid in quantitative yield. This material crystallised from acetone-benzene in compact, yellow prisms or long, yellow needles; these specimens, when left in a desiccator, changed into a colourless modification dissolving in acetone to a yellow solution, from which the yellow forms were recovered. Both varieties melted at 140—141° with blackening: 0·1793 gave 0·1257 CO_2 and 0·0427 H_2O, C = 19·13, H = 2·66; 0·1903 gave 0·0978 Te, Te = 51·39. $C_4H_6O_4Te$ requires C = 19·56, H = 2·46, Te = 51·92%.

Tellurodiacetic acid was readily soluble in water, alcohol, or ether, moderately soluble in ethyl acetate or acetone, but almost insoluble in benzene, chloroform, or light petroleum. Its solutions were pale yellow and from water or ethyl acetate it separated with solvent of crystallisation which in the latter case was held tenaciously. These solvated crystals were yellower and had a lower melting point.

Solutions of tellurodiacetic acid in water or ethyl acetate oxidised slowly to a colourless, amorphous, insoluble oxide, a change which was promoted by hydrogen peroxide but inhibited by a trace of sulphur dioxide. The acid blackened in presence of hydrochloric acid, but was stable to warm aqueous alkalis, and decomposed carbonates.

The following salts were prepared: *diammonium* salt, sulphur-yellow powder decomposing at 135°, *disodium* salt, yellow, both soluble in water; *disilver* salt, white, amorphous, insoluble substance, stable to light; *copper* salt, light green precipitate.

When suspended in chloroform and treated with chlorine, tellurodiacetic acid reverted to dichlorotelluridiacetic acid.

Ditellurodiacetic Acid (VII).—A mixture of 10·4 g. of tellurium tetrachloride, 6·6 g. of acetic anhydride, and 70 c.c. of dry chloroform was heated under reflux for 4 hours, until the initially delayed evolution of hydrogen chloride had nearly ceased and the tetrachloride had dissolved. The clear orange-yellow solution, decanted from 0·2 g. of tellurium, was evaporated at the ordinary temperature in a vacuum desiccator to a viscid yellow oil which, when stirred with chloroform, gave a crop of grey, flocculent material. The product, weighing 3·3 g. after drying in a vacuum desiccator, melted indefinitely at 100° and was permanently deliquescent. It was never, however, quite homogeneous and consisted mainly of acetanhydrobistelluritrichloride, $TeCl_3{\cdot}CH_2{\cdot}CO{\cdot}O{\cdot}CO{\cdot}CH_2{\cdot}TeCl_3$,

which on exposure to moisture was transformed first to trichlorotelluriacetic acid, $TeCl_3 \cdot CH_2 \cdot CO_2H$, and then to hydroxylation products of this acid.

By reduction of this material with potassium metabisulphite (6 mols. to 1 mol. of anhydrobistrichloride), sulphur dioxide was evolved, and *ditellurodiacetic acid* was obtained in quantitative yield, partly precipitated and partly by ether extraction of the deep yellow solution. Purification was effected by crystallisation from acetone or acetone-benzene containing a little sulphur dioxide, when lustrous, orange-red to ruby-red prisms were obtained, which became discoloured at 140° and blackened at 144°: 0·1390 gave 0·0648 CO_2 and 0·0247 H_2O, C = 12·72, H = 1·99; 0·1546 gave 0·1054 Te, Te = 68·19. $C_4H_6O_4Te_2$ requires C = 12·87, H = 1·62, Te = 68·33%.

In water ditellurodiacetic acid was more sparingly soluble than tellurodiacetic acid, but the former dissolved more readily in ethyl acetate; it was also soluble in acetone or alcohol, but was insoluble in chloroform, benzene, or light petroleum. Ditellurodiacetic acid dissolved to orange or orange-red solutions, in which it became oxidised, on exposure, to an insoluble, amorphous oxide. It gave soluble, yellow alkali salts, a light green copper salt, and an orange silver salt, the last two being insoluble; the silver compound blackened on exposure to light. When suspended in chloroform, it combined additively with chlorine or bromine, the bromide being a yellow solid.

The oily mother-liquor from the preparation of the foregoing trichlorotellurium compounds yielded 1 g. of methylenebistelluritrichloride and a smaller amount of an unidentified substance (nacreous leaflets, m. p. 175° with decomp.) stable to moist air and giving a red telluriferous reduction product.

When in the preceding condensation the proportion of acetic anhydride was increased to 2 molecules and that of chloroform decreased to 4 c.c. per g. of tellurium tetrachloride, the deliquescent, grey solid obtained (6·5 g. from 18·5 g. of $TeCl_4$) melted near 130° and consisted of a mixture of di- and tri-chlorotellurium compounds, since on reduction it yielded only telluro- and ditelluro-acetic acids. This mixture contained Cl = 30·63 and Te = 41·88%, showing that the substance which by reduction furnished ditellurodiacetic acid must have one of the related formulæ, $TeCl_3 \cdot CH_2 \cdot CO_2H$ or $TeCl_3 \cdot CH_2 \cdot CO \cdot O \cdot CO \cdot CH_2 \cdot TeCl_3$, the junction of two tellurium atoms occurring, therefore, on reduction.

Methylenebistelluritrichloride (VIII).—The chloroform filtrates from the above-mentioned grey solid, when concentrated and left in a vacuum, slowly deposited large, brittle, prismatic crystals

of almost pure *methylenebistelluritrichloride* (2·3 g.). Recrystallised from dry chloroform with exclusion of moist air, it separated in colourless, transparent prisms, often of acicular habit, and melting at 173° with effervescence and formation of a red liquid. The latter property distinguishes this substance from the other tellurium compounds derived from acetic anhydride. That this product was not changed in composition by recrystallisation was shown by the following data: (i) original preparation: 0·1853 gave 0·0179 CO_2 and 0·0103 H_2O, C = 2·64, H = 0·62; 0·1004 gave 0·1782 AgCl, Cl = 43·91; 0·2207 gave 0·1179 Te, Te = 53·42; (ii) recrystallised material: 0·4153 gave 0·0380 CO_2 and 0·0194 H_2O, C = 2·50, H = 0·52. $CH_2Cl_6Te_2$ requires C = 2·49, H = 0·42, Cl = 44·16, Te = 52·93%.

Methylenebistelluritrichloride was slowly changed by moist air with evolution of hydrogen chloride and hydrolysed immediately by cold water to white, amorphous oxide or oxychloride. Successive treatment with aqueous caustic potash and nitric acid produced an aldehydic odour. The trichloride condensed readily with methyl ketones.

Methylenebistelluriacetone Dichloride (X).—When boiled under reflux with chloroform containing a small proportion of acetone, the preceding bistrichloride evolved hydrogen chloride and on cooling the solution the diacetone condensation product separated in quantitative yield. Recrystallised from chloroform containing acetone, the substance was obtained in lustrous, transparent, colourless, prismatic needles, stable in moist air, m. p. 181° (decomp.): 0·1510 gave 0·0870 CO_2, 0·0333 H_2O, C = 15·72, H = 2·47; 0·0724 gave 0·0790 AgCl, Cl = 27·00. $C_7H_{12}O_2Cl_4Te_2$ requires C = 16·01, H = 2·30, Cl = 27·02%. A similar crystalline condensation product was obtained with acetophenone and accordingly it is likely that the reaction with ketones and allied compounds is capable of further extension.

Ditelluromethane (IX).—Finely-powdered methylenebistelluritrichloride (0·33 g. or 1 mol.) was mixed with 0·92 g. (6 mols.) of potassium metabisulphite and 10 c.c. of cold water. Sulphur dioxide was evolved and *ditelluromethane* was produced as a dark red, amorphous powder which, after washing with cold water, was dried in a vacuum (yield quantitative). This red substance changed slowly at the ordinary temperature, but rapidly at or above 30°, to a black modification which melted gradually from 50 to 90° without decomposition, forming viscous, pitch-like drops. On cooling, this pitch resolidified to a dense, brittle solid having a silvery lustre and resembling a heavy fusible metal. This modification was analysed: 0·1463 gave 0·0237 CO_2 and 0·0133 H_2O;

C = 4·42, H = 1·02; 0·1706 gave 0·1606 Te, Te = 94·14 (total 99·58). CH_2Te_2 requires C = 4·46, H = 0·75, Te = 94·79 %.

When heated to a high temperature in air, ditelluromethane exploded with a brilliant bluish-green flash, evolving garlic odours and leaving a residue of tellurium. Ditelluromethane was insoluble in water or organic media. When suspended in chloroform, it absorbed chlorine, regenerating methylenebistelluritrichloride, and combined with bromine to form a yellow bromide intumescing violently at 214°.

The authors desire to express their thanks to Messrs. Brunner Mond and Company, Ltd., and to the Government Grant Committee of the Royal Society for grants which have helped to defray the expense of this research.

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[*Received, January 15th,* 1925.]

LXXVII.—*The Influence of Valency Direction on the Dissociation Constants of Dibasic Acids.*

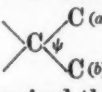
By CLAUDE HYMAN SPIERS and JOCELYN FIELD THORPE.

As the outcome of work described in numerous papers, the hypothesis has been advanced that the angle between any two valencies of a carbon atom can be profoundly altered in at least two ways:

(1) by altering the volume of the groups attached to the other two valencies;

(2) by inclusion of these two valencies in a ring complex, the internal angle of which can be assumed to be fixed.

Until recently, the evidence adduced in support of this hypothesis has been purely chemical. For example, it has been shown that an alteration in valency direction brought about in the ways above mentioned influences the ease of formation and the stability of ring systems, *e.g.*, of β-lactones (Bains and Thorpe, J., 1923, **123**, 2742), and also determines whether ring-chain tautomerism shall occur in certain cases (see *ibid.*, p. 2865). In Part XI (J., 1924, **125**, 2524) of the series of papers on ring-chain tautomerism, Dutt and one of us have used a physical method to demonstrate the shifting of equilibrium between the tautomeric coloured and colourless forms of the fluoresceins and rhodamines, produced by alteration of valency direction. The work now described shows the effect of this alteration by another physical method.

The diminution of the angle produced in either of the above ways must tend to cause the approximation of the carbon atoms (*a*) and (*b*),  and of any groups attached to them. It has long been recognised that the primary and secondary dissociation constants of dibasic carboxylic acids are largely determined by the distance between the carboxyl groups; the greater this distance, the smaller the primary constant and the greater the secondary constant. The cases of the oxalic acid series and the geometrically isomeric maleic and fumaric acids may be quoted in illustration. It is at once apparent that an alteration of the angle between two valencies of an atom which forms one of a chain of atoms connecting two carboxyl groups will show itself by an alteration in dissociation constant. Malonic, succinic, and glutaric acids form a good series of derivatives which can be utilised in studying this effect. Table I gives the dissociation constants of various β-substituted glutaric acids, which have now either been determined or redetermined by us. It also shows the equilibrium reached when keto- or ring-hydroxy-acids of the types I and II are heated in aqueous potash to 145°.

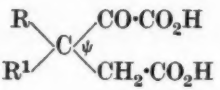
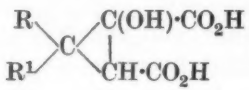
(I.)   (II).

TABLE I.

	Substituent.	Calc. value of ψ.	Equilibrium mixture. % Keto.	% Enol.	$K_{25} \times 10^5$.
1.	H,H	115·3°	100	0	4·69
2.	Me,H	112·5	—	—	6·00
3.	Et,H	?	—	—	5·29
4.	$(CH_2)_4$ (*cyclo*pentane ring).	109·7	100	0	17·3
5.	Me,Me	109·5	100	0	19·8
6.	Me,Et	?	100	0	24·4
7.	Et,Et	?	38	62	33·9
8.	Pr,Pr	?	29	71	33·9
9.	$(CH_2)_5$ (*cyclo*hexane ring).	107·2	0	100	33·4
10.	$(CH_2)_6$ (*cyclo*heptane ring).	105·3	Behaviour intermediate between that of 4 and 9.		39·5

It will be seen that the introduction of *gem*-groupings causes a remarkably large increase in dissociation constant, ββ-dipropylglutaric acid being several times stronger than glutaric acid, whereas the variation in dissociation constant produced by introducing alkyl groups into the various fatty acids is nothing like as great, as can be seen from Table II.

TABLE II.

$K_{25} \times 10^5$.

Formic acid	21·4				
Acetic acid	1·80				
Propionic acid	1·34				
n-Butyric acid	1·52	Dimethylacetic acid	1·43	Trimethylacetic acid	0·98
n-Valeric acid	1·50	Methylethylacetic acid	1·68	Dimethylethylacetic acid	0·96
n-Hexoic acid	1·38	Diethylacetic acid	1·95		
Heptoic acid	1·31	Ethylpropylacetic acid	1·97*		
		*iso*Propylacetic acid	1·67		

* Determined by us.

Large increases of dissociation constant are also produced in the malonic and succinic acids by similar changes in structure (see below), but the hypotheses which have hitherto been advanced to explain the relationships between chemical constitution and acidity throw no light on the mechanism causing the large effects now discussed. On the one hand, it is not yet possible to apply successfully modern electrical theories of valency and the structure of atoms and molecules, even to the most simple cases of substitution (compare Lewis, "Valence and the Structure of Atoms and Molecules," 1923, chap. VIII; Thompson, *Phil. Mag.*, 1923, [vi], **46**, 497). On the other hand, generalisations which have been deduced empirically without consideration of the inner structure of atoms and molecules present many difficulties. Of the various attempts to explain the effects of substitution on these lines, Flürscheim's seems to have gained the greatest currency. This author considers the effect of a substituent to be the result of the operation of three factors—the "polar," "quantitative," and "steric" factors—the magnitude of each of which can be estimated by independent experiments. He claims to be able to predict whether a substituent will increase or decrease the dissociation constant of an acid into which it is introduced and also the order of magnitude of the effect. He predicts, for example, that methylethylacetic acid should be stronger than dimethylacetic acid but weaker than diethylacetic acid. However, here the so-called "steric" factor, the value of which is estimated from esterification experiments, is much more important than the other two factors. Since no explanation is offered as to how this steric influence is produced, the theory is of small utility, as it stands (compare Derick, *J. Amer. Chem. Soc.*, 1911, **33**, 1167). The present theory suggests a mechanism whereby part, at least, of this steric effect is produced.

The alkylated glutaric, malonic, and succinic acids will now be discussed in detail, although it should be pointed out that the present paper is mainly concerned with the remarkable effects produced by

gem-groupings. The introduction of *gem*-groups into malonic acid or into glutaric acid in the ββ-position leaves the symmetry of the molecule unaltered. There is thus no free rotation effect to be considered and the acids of each series are strictly comparable with one another. The same applies to succinic acid, although the symmetry of the molecule is modified slightly. The present theory must, in addition, apply where only one alkyl group is introduced, for, here also, a change in valency direction results. In the case of succinic acid, since the alkyl group is necessarily attached to the same carbon atom as a carboxyl group, there will doubtless be a marked free rotation effect. The effect of substitution will be considered under two heads :

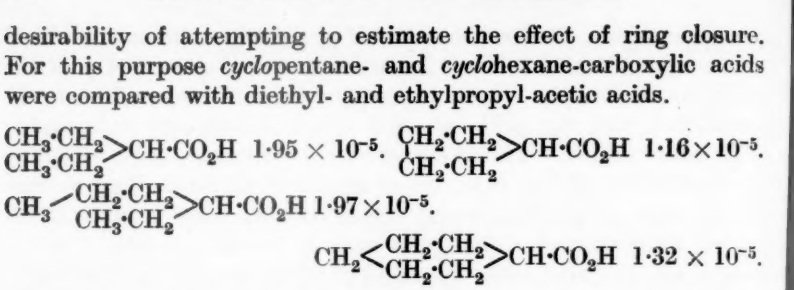
(1) the " general " effect, the magnitude and sign of which are estimated from the monobasic acids, and

(2) the " approach " effect, which is mainly brought about by altered valency direction.

The Glutaric Acids.

On the whole, the same result is reached whether we arrange the different groupings according to the magnitude of their effects on the dissociation constant of glutaric acid or according to their influence in causing ring-chain tautomerism of the kind above indicated. From Table II we see that the introduction of alkyl groups into the β-position in propionic acid causes a slight rise in acidity, the effect of the methyl group being the greatest. That the glutaric acids with a *gem*-grouping should be so very much stronger than the monosubstituted acids and that the diethyl acid should be stronger than the dimethyl acid, although the monoethyl acid is weaker than the monomethyl acid, is remarkable evidence of the volume effect in altering valency direction. Dipropylglutaric acid is very slightly soluble in water, and from the results obtained it is difficult to say whether it is stronger than the diethyl acid. However, from the chemical evidence one would not expect a very great difference between the two acids. As was expected, *cyclo*pentanediacetic acid is weaker than dimethylglutaric acid, although perhaps the difference is somewhat large. *cyclo*Hexanediacetic acid, contrary to expectation, is weaker than dipropylglutaric acid. The experiments of Ingold and Baker (J., 1923, **123**, 122) seemed to indicate that the *cyclo*heptane ring was less effective than the *cyclo*hexane ring in diminishing the tetrahedral angle; on the other hand, the electrical measurements suggest the reverse, as one would anticipate, were the *cyclo*heptane ring, like the *cyclo*hexane ring, to lie in one plane. These anomalies in the cyclic acids suggested the

desirability of attempting to estimate the effect of ring closure. For this purpose *cyclo*pentane- and *cyclo*hexane-carboxylic acids were compared with diethyl- and ethylpropyl-acetic acids.



Thus ring closure in a simple acid causes a considerable decrease in dissociation constant, and this may explain why *cyclo*hexanediacetic acid is weaker, instead of stronger, than dipropylglutaric acid; it may also explain the somewhat large difference in strength between *cyclo*pentanediacetic acid and dimethylacetic acid.

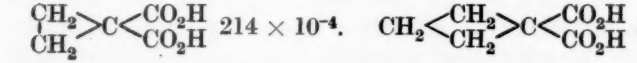
The Malonic Acids.

TABLE III.

$K_{25} \times 10^4$.

Malonic acid	16·3				
Methylmalonic	8·6				
Ethylmalonic	12·7	Dimethylmalonic	7·6		
n-Propylmalonic	11·5	Methylethylmalonic	16·1		
n-Butylmalonic	11·6	Methyl-*n*-propylmalonic	21·2	Diethylmalonic	74
		Methyl-*n*-butylmalonic	20·3	Ethyl-*n*-propylmalonic.	116
				Ethyl-*n*-butylmalonic.	116
				Dipropylmalonic.	119

The introduction of one alkyl group has the same effect in malonic acid as in acetic acid—it acts as a positive group. A second small alkyl group also lowers the dissociation constant, but as the size of the alkyl group is increased the positive effect of the group is neutralised and reversed by the approximation of the carboxyl groups due to altered valency direction. The two *cyclo*paraffin dicarboxylic acids present an anomaly, for the acid with the larger ring is weaker than the acid with the smaller ring.



The substituent is here necessarily differently situated with respect to each of the two carboxyl groups. Table II shows that an alkyl group introduced in the α- or β-position into propionic acid causes a slight increase in acidity. Thus an alkyl group may be expected to raise slightly the dissociation constant of either carboxyl group. The remarkable effect of the *gem*-dimethyl group is seen by comparing

TABLE IV.

1. Succinic acid 6·6
2. Methylsuccinic acid 8·6
11. *s*-Dimethylsuccinic acid 12·3 } 19·1 }
3. Ethylsuccinic acid 8·8
5. *aa*-Dimethylsuccinic acid 8·2
12. *s*-Methylethylsuccinic acid. 20·1 } 20·7 }
4. *n*-Propylsuccinic acid 8·8
6. *a*-Methyl-*a*-ethylsuccinic acid 9·5
7. Trimethylsuccinic acid 30·7
14. *s*-Diethylsuccinic acid 24·5 } 34·3 }
13. *s*-Methylpropylsuccinic acid 27·1 } 33·5 }
8. Dimethylethylsuccinic acid 55·6
10. Tetramethylsuccinic acid 31·4
9. Dimethyl-*n*-propylsuccinic acid 55·1
15. *s*-Dipropylsuccinic acid 25 } 29 }

NOTE.—The symmetrical acids exist in two forms.

acids 2 and 7, 3 and 8, 4 and 9, and 5 and 10 (Table IV). Two alkyl groups produce a greater effect when attached to two different carbon atoms than when attached to the same atom. The above tables show that increase in the size of the groups beyond a certain limit produces very little or no further effect; this limit is reached with the ethyl or propyl group.

EXPERIMENTAL.

No details of the preparations of the various acids are given, since these are to be found in the literature. The two acetic acids were prepared from the corresponding malonic acids; the propyl iodide required for ethylpropylacetic acid was made from propyl alcohol obtained by the catalytic reduction of allyl alcohol. The *cyclo*pentane- and *cyclo*hexane-carboxylic acids were prepared from the corresponding bromides by the Grignard reaction. These four acids were purified by repeated fractionation in a vacuum, the portions used in the measurements being collected over a range of less than 0·5°. The solid acids were crystallised until their melting points were at least as high as those recorded in the literature and were constant. After the dissociation constant had been determined, each acid was again crystallised or distilled and the constant redetermined; in no case was an appreciable difference found.

The initial solutions were prepared from the required amounts of the acids, and the dilutions were made in the cell. The conductivities were determined at 25° by the Kohlrausch method, no attempt being made to achieve a degree of accuracy beyond that attainable with the ordinary apparatus. The results are corrected

for the conductivity of the water used; this was in the neighbourhood of $1{\cdot}5 \times 10^{-6}$ reciprocal ohm.

Acid.	Dilution (litres).	No. of determns.	Limits of $K \times 10^5$.	Mean $K \times 10^5$.	Other determinations.
Glutaric	16–1024	7	4·66–4·71	4·69	4·71. Voermann, *Rec. trav. chim.*, 1904, **23**, 265.
β-Methylglutaric	33·46–1070·72	6	5·97–6·05	6·00	5·93. Walden, *Z. physikal. Chem.*, 1891, **8**, 433.
β-Ethylglutaric	32·56–1041·92	6	5·28–5·36	5·29	
ββ-Dimethylglutaric	31·33–1002·56	6	19·5–20·0	19·8	20·0. Walker, *Annalen*, 1896, **292**, 146.
ββ-Methylethylglutaric	31·53–1008·96	6	24·2–24·6	24·4	
ββ-Diethylglutaric	32–1024	6	33·7–35·0	34·4(33·9*)	
ββ-Dipropylglutaric	512–2048	3	32·7–34·2	(33·9*)	
*cyclo*Pentane-1 : 1-diacetic	127·2–2035·2	5	17·0–17·6	17·3	
*cyclo*Hexane-1 : 1-diacetic	256–1024	3	33·3–34·2	33·7(33·4*)	
*cyclo*Heptane-1 : 1-diacetic	279·6–1118·4	3	38·9–40·2	39·5	
Diethylacetic	31·38–1004·16	6	1·92–1·97	1·95	2·03. Billitzer, *Monatsh.*, 1899, **20**, 666.
Ethylpropylacetic	38·74–1239·68	6	1·94–2·01	1·97	
*cyclo*Pentanecarboxylic	26·77–856·64	6	1·14–1·18	1·16	1·24. Zelinsky and Isgaryschev, *J. Russ. Phys. Chem. Soc.*, 1908, **40**, 1379.
*cyclo*Hexanecarboxylic	64·91–1038·56	5	1·27–1·37	1·32	1·34. *Idem, ibid.*

* Mean of the values at dilutions 512 and 1024.

Zelinsky and Isgaryschev (*loc. cit.*) used unplatinised instead of platinised electrodes, owing to a wandering of the minimum. No difficulty was experienced by the present authors with platinised electrodes.

We are indebted to the Chemical Society for a grant which met part of the expense of this investigation.

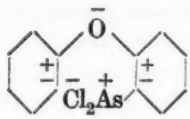
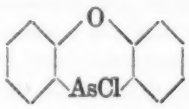
IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
SOUTH KENSINGTON, S.W. 7. [*Received, January 8th*, 1925.]

LXXVIII.—6-*Chlorophenoxarsine.*

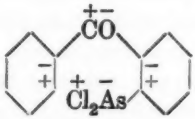
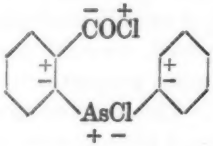
By EUSTACE EBENEZER TURNER and ARTHUR BRAXTON SHEPPARD.

ONE of us, while working in 1918 with Sir William Pope, obtained from arsenic trichloride and diphenyl ether a condensation product (then called *As*- or 6-chlorophenoxarsine) to which formula II was assigned. This formula was subsequently adopted by Lewis, Lowry, and Bergeim (*J. Amer. Chem. Soc.*, 1921, **43**, 890).

The present communication describes the synthesis of 6-chlorophenoxarsine by a method which establishes its constitution, namely, by the elimination of hydrogen chloride from o-*phenoxyphenyldichloroarsine* (I):

(I.)  (II.) 

This conversion takes place with great readiness, for example, when one attempts to distil the dichloroarsine under diminished pressure. This result, surprising at first, is in full accord with the theory of alternate latent polarities, which, incidentally, appears to explain why Aeschlimann and McCleland (J., 1924, **125**, 2025) failed to effect ring-closure with benzophenone-*o*-dichloroarsine (III) or the acid chloride (IV) of *o*-carboxydiphenylchloroarsine, and may also account for the comparative ease with which arsenic trichloride condenses with diphenyl ether, and the even greater ease with which it condenses with diphenylamine.

(III.)   (IV.)

It seems justifiable to assume that in the above cases it is the element connecting the two benzene nuclei which acts as the key atom. In this connexion, it is important to note that arsenic trichloride and diphenyl ether do not interact in absence of aluminium chloride.

Experimental.

o-*Nitrodiphenyl ether* was prepared from *o*-chloronitrobenzene by a modification of the method used by Haeussermann and Teichmann (*Ber.*, 1896, **29**, 1446). It was not found advantageous to use *o*-bromonitrobenzene, proposed by Ullmann (*ibid.*, p. 1878), whose method involves, also, the use of metallic potassium.

The liquid obtained by heating together potassium hydroxide (1 mol.) and water (0·6 mol.) was mixed with phenol (1 mol.) and a little copper powder, a mixture of phenol (1 mol.) and *o*-chloronitrobenzene (1 mol.) being added. The mixture was heated under reflux for 6 hours, the temperature being slowly raised from 150° to 210°. The cooled product was treated with water, extracted with ether, and the ethereal solution extracted with alkali. By evaporating the dried solvent, and distilling under diminished pressure, *o*-nitrodiphenyl ether was obtained in 85% yield.

o-*Aminodiphenyl Ether*.—Ullmann (*loc. cit.*), in preparing this compound by reduction of the nitro-compound with alcoholic stannous chloride, isolated the double tin salt and decomposed this

with hydrogen sulphide, apparently because Haeussermann and Teichmann (*loc. cit.*), using alkali to remove tin, were unable to isolate the amine. The following method, however, gave good results: the double tin salt, obtained by Ullmann's method, was dissolved in water, and treated below 0° with a large excess of potassium hydroxide. The resulting purple oil was extracted with ether, and the product distilled (b. p. 160—162°/12—15 mm.). The amino-compound, without further purification, melted at 41·5° (Found: N = 7·6; calc., N = 7·56%).

The *benzoyl* derivative forms white needles, m. p. 75° (Found: N = 4·9. $C_{19}H_{15}O_2N$ requires N = 4·84%).

o-*Phenoxybenzeneazo*-β-*naphthol*, obtained in the usual manner, separates from alcohol or glacial acetic acid in bright red needles, m. p. 135° (Found: N = 8·3. $C_{22}H_{16}O_2N_2$ requires N = 8·24%).

o-*Phenoxyphenylarsinic acid* and o-*phenoxyphenyldichloroarsine* were prepared as follows: The diazotised amine was slowly added to a well-stirred, ice-cold solution of arsenious oxide in sodium carbonate (usual proportions), a little copper sulphate being added at intervals. The temperature was finally raised to 50°, tar removed, and an excess of hydrochloric acid added. The arsinic acid separated as colourless needles. Owing to the small amount of material available, a little of the acid was collected, crystallised from water, and analysed (Found: M = 295, by titration with alkali. $C_{12}H_{11}O_4As$ requires M = 294), the acid suspension of the main bulk being saturated with sulphur dioxide in presence of a little iodine. The dichloroarsine separated as an orange-red oil, which was isolated by means of carbon tetrachloride. On attempting to distil it at 10 mm. pressure, it was completely converted into 6-chlorophenoxarsine, the colourless prisms obtained not depressing the m. p. (122°) of a specimen prepared from diphenyl ether and arsenic trichloride [Found: Cl = 12·7; As = 26·9; M (in boiling acetone) = 277. $C_{12}H_8OClAs$ requires Cl = 12·7; As = 26·9%; M = 279].

Note on the preparation of diphenyl ether. The preparation of the ether by the method described by Hirsch (*Ber.*, 1890, **23**, 3707; "Fortschritte," Friedlaender, III, 51) has been very fully investigated. Under no conditions was a yield of over 20% obtained, calculated on the aniline used.

Phenyl carbonate, heated under reflux with an equal weight of acetic anhydride for 14 hours, was quantitatively converted into phenyl acetate, no diphenyl ether being obtainable in this way: $(PhO)_2CO + Ac_2O = 2AcOPh + CO_2$.

Action of Aluminium Chloride on Diphenyl Sulphide [With H. S. Bolton].—In an attempt to obtain the sulphur analogue of 6-chloro-

phenoxarsine, arsenic trichloride, diphenyl sulphide, and aluminium chloride (anhydrous) were heated together at 175—185°. Hydrogen chloride was evolved for some time, and the product was then cooled, treated with ice, then with hydrochloric acid, and extracted with ether. The latter contained only diphenylene disulphide (Found: C = 66·5; H = 3·7; calc., C = 66·7; H = 3·7%). When diphenyl sulphide was heated with aluminium chloride, benzene was obtained as one product, together with diphenylene disulphide, possibly formed as follows: (*a*) $SPh_2 + HCl = PhH + PhSCl$; (*b*) $2PhSCl = Ph{\cdot}Ph + S_2Cl_2$; (*c*) $Ph{\cdot}Ph + S_2Cl_2 = C_{12}H_8S_2 + 2HCl$. These changes are assumed to occur only in presence of aluminium chloride (compare Friedel and Crafts, *Ann. chim. phys.*, 1884, [vi], **1**, 530).

The Gas Light and Coke Company kindly supplied some of the *o*-chloronitrobenzene used in this investigation, and the authors desire to thank them and Mr. W. Gordon Adam of the Beckton Works for this gift.

EAST LONDON COLLEGE,
UNIVERSITY OF LONDON. [*Received, December 11th*, 1924.]

LXXIX.—*A Determination of the Melting and Transition Points of Potassium Dichromate.*

By PERCY LUCOCK ROBINSON, GEORGE EDWARD STEPHENSON, and HENRY VINCENT AIRD BRISCOE.

IN the course of another investigation, it was necessary to fuse recrystallised potassium dichromate in order to eliminate traces of organic matter, and our attention was thus drawn to the behaviour of the molten salt on cooling.

Mitscherlich (*Ann. Phys. Chem. Pogg.*, 1833, **28**, 120) stated that the crystals obtained from molten potassium dichromate, which he supposed to be identical with those separating from aqueous solution, "fall rapidly to a powder" on cooling. The change is so striking as to suggest immediately that a transition to another form has occurred, but we could find no description of the phenomenon in English text-books and thus were led to investigate the matter further. Lehmann (*Molekularphysik*, 1888, **1**, 172) observed the change under the microscope, and Wyrouboff (*Bull. soc. franç. min.*, 1890, **13**, 277), on the evidence of the change in extinction angle of the crystals on cooling, concluded that potassium dichromate existed in three forms, a "*clinorhombique*" form stable at temperatures near the melting point, a triclinic form stable at the ordinary temperature, and a second triclinic form stable within a narrow

range of temperature between its transition points into the other forms. These transition points were not determined.

Tammann ("Kristallisieren und Schmelzen," 1903, p. 40) found that the breakdown of the crystalline solid occurred at a definite temperature, 240°, but without thermal effect. Schemtschuschny (*Zeit. anorg. Chem.*, 1908, **57**, 267), in an account of the system KCl–$K_2Cr_2O_7$, gave 397° as the melting point and 236° as the transition point.

It is the purpose of this paper to record a description of the phenomenon accompanying the solidification and cooling of potassium dichromate and of a determination of the melting and transition points.

Experimental.

Fused potassium dichromate crystallises as a compact cake of large, dark brownish-red, tabular crystals, with a marked reduction in volume shown by the shrinkage of the still fluid portion into the interstices between the crystals, leaving a pitted surface on complete solidification. On further cooling, the crystals change to a loose, orange-red powder, occupying a greater volume than the original solid. Should the conditions be such that this change takes place before the whole of the melt beneath the crust has solidified, the expansion attending it often causes some of the fluid to well out in volcanic fashion through the crust. The line separating the orange border and the dark compact mass is very sharp and obviously isothermal in character, as it conforms to the shape of the containing vessel.

The sharpness of the change is readily demonstrated by gathering the liquid on the end of a glass rod, allowing it to set, and, when the first signs of transition show at the edge, blowing gently upon it; the whole mass at once changes colour, breaks up, and falls off the rod. This is so striking as to afford a good lecture experiment in illustration of transition between dimorphic forms, and if a thermometer be used in place of the rod an approximate indication of the transition temperature is obtained.

A similar experiment with fused anhydrous sodium dichromate shows neither colour change nor tendency to loosen from the rod; though this salt of course lightens in colour if kept at the ordinary temperature long enough to permit its hydration by atmospheric moisture.

The thermometric method was chosen as the readiest means of fixing more precisely the transition temperature of potassium dichromate. As the expansion on cooling invariably burst glass test-tubes, the salt, which had been recrystallised, dried, and fused, was melted in a cylindrical copper vessel, heated electrically and

very well lagged. By suitably controlling the current supplied, any desired rate of cooling was attained. The thermometer was placed in a mercury bath contained in a narrow test-tube of stout glass immersed in the melt, and was thus protected from the compressive effect of this expansion, which could otherwise cause an apparent lag in temperature. Time intervals for each degree fall of the temperature were taken by means of two stop-watches, worked alternately, the thermometer being observed with a microscope. In this manner, a number of cooling curves for potassium dichromate and sodium dichromate were obtained. These made it apparent that sodium dichromate shows no arrest in cooling over the range 300—70°, while potassium dichromate shows a single well-marked arrest at 241° over a similar range.

The thermometer had been compared with a standard and the correction for exposed stem was applied.

As the transition temperature, 241°, is appreciably higher than Schemtschuschny's determination by use of a thermo-couple, it was decided to repeat the work using some other method of measurement. For this purpose a platinum resistance thermometer, in conjunction with a Callendar and Griffiths Bridge and a Hartmann and Braun moving-coil galvanometer, was substituted for the mercury-in-glass thermometer. The porcelain sheath covering the resistance element was immersed directly in the molten salt, contained in this case in a stout glass tube. The scale was arranged so that one division of the galvanometer scale, which could be read to tenths of a division, was equivalent to about 0·7°. To observe the rate of fall in temperature, the time taken for the light-spot to move over a division was measured, using two stop-watches as before. At the arrests, however, the resistance of the platinum was balanced against the bridge by bringing the light-spot to the previously noted zero point on the scale.

In this manner, the results obtained were (*a*) for the melting point 398·4° $\pm$ 0·5° (mean of five determinations) and (*b*) for the transition point 236·8° $\pm$ 0·5° (mean of seven determinations).

These results are accepted as correct to the exclusion of those obtained with the mercury thermometer.

One of the authors (G. E. S.) desires to acknowledge a grant from the Department of Scientific and Industrial Research, enabling him to take part in this investigation.

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NEWCASTLE-UPON-TYNE. [*Received, January 24th,* 1925.]

LXXX.—*The Reactivity of Antimony Halides with certain Aromatic Compounds. Part II.*

By ERNEST VANSTONE.

THE investigation by thermal analysis of binary systems containing antimony halides provides a useful method of tracing the conjugation of the residual affinity of unsaturated atoms or groups with that of the phenyl groups in compounds of the type Ph·α·α·Ph (J., 1914, **105**, 1491). The behaviour of certain compounds of the type Ph·α·β·Ph has now been investigated. The present paper deals with the systems (1) antimony trichloride–benzanilide, (2) antimony tribromide–benzanilide, (3) antimony trichloride–benzylaniline, and (4) antimony tribromide–benzylaniline.

Most aromatic compounds containing one benzene nucleus combine with 2 mols. of antimony halides, *e.g.*, $2SbCl_3,C_6H_6$. *s*-Diphenylethane and azobenzene combine with 4 mols. of the antimony compounds. The systems with benzylaniline have behaved otherwise and given results quite different from those obtained with any of the systems so far investigated.

EXPERIMENTAL.

Benzanilide and Antimony Halides (With W. G. MESSENGER).

The Systems (1) *Benzanilide–Antimony Trichloride*, (2) *Benzanilide–Antimony Tribromide.*—The pure substances are colourless; the mixtures were dark red in the liquid state and reddish-brown in the solid. The mixtures, the freezing points of which were determined as described in previous papers, could be made to solidify only by seeding with the solid phase.

The diagrams (Fig. 1) representing these systems consist of four branches and show that in each system two stable compounds are formed having the composition $2SbX_3,NHPh·COPh$ and $SbX_3,NHPh·COPh$, respectively. The maxima are at 33·3 and 50% of $SbCl_3$ and 99° and 112°, respectively. These temperatures are the melting points of the compounds. It will be observed that for the mixture containing 59·32% of benzanilide, the portion of the curve below the eutectic has been obtained.

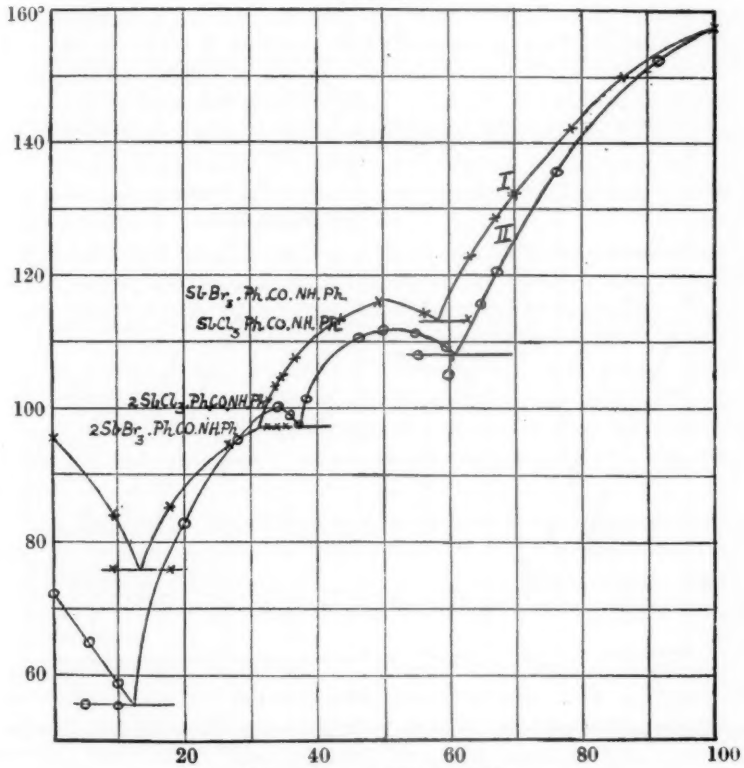
The system containing the tribromide has only one maximum point, namely, at 50% and 116°, the melting point of the compound $SbBr_3,NHPh·COPh$. The other compound, $2SbBr_3,NHPh·COPh$, is unstable, decomposing before its melting point is reached.

The above diagrams show that benzanilide, a compound containing two benzene nuclei, behaves like a compound with one nucleus only. Its reactivity towards antimony halides is nearly

equal to that of toluene. This can be seen by comparing the compounds formed :

Toluene.	Benzanilide.
$Ph\cdot CH_3,2SbCl_3$ stable.	$Ph\cdot CO\cdot NHPh,2SbCl_3$ stable.
$Ph\cdot CH_3,SbCl_3$,,	$Ph\cdot CO\cdot NHPh,SbCl_3$,,
$Ph\cdot CH_3,2SbBr_3$,,	$Ph\cdot CO\cdot NHPh,2SbBr_3$ unstable.
$Ph\cdot CH_3,SbBr_3$,,	$Ph\cdot CO\cdot NHPh,SbBr_3$ stable.

FIG. 1.



Mols. of benzanilide per 100.

I *Antimony tribromide–benzanilide.* II *Antimony trichloride–benzanilide.*

It is possible also to compare the reactivity of the groups $Ph\cdot CH_2\cdot$, $Ph\cdot NH\cdot$, and $Ph\cdot CO\cdot$ with that of toluene, $Ph\cdot CH_3$.

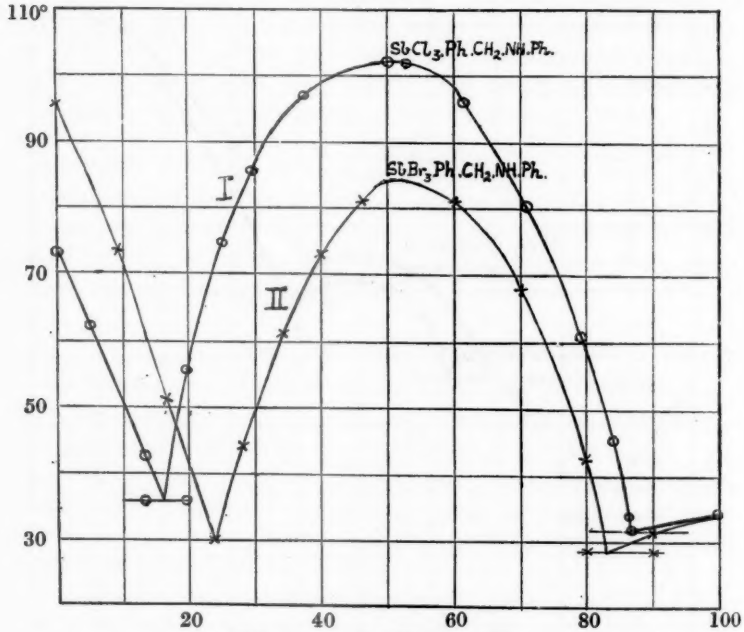
Group.	Combination with $SbCl_3$.	Combination with $SbBr_3$.
$Ph\cdot CH_3$	$Ph\cdot CH_3,2SbCl_3$	$Ph\cdot CH_3,2SbBr_3$
	,, ,$SbCl_3$	,, ,$SbBr_3$
$Ph\cdot NH\cdot$	$Ph\cdot NH,2SbCl_3$	$Ph\cdot NH,2SbBr_3$ unstable
	,, ,$SbCl_3$	$Ph\cdot NH,SbBr_3$
$Ph\cdot CH_2\cdot$	$Ph\cdot CH_2,2SbCl_3$	$Ph\cdot CH_2,2SbBr_3$
	,, ,$SbCl_3$	—
$Ph\cdot CO\cdot$	None	None

Systems containing Benzylaniline.

Benzylaniline–Antimony Trichloride and Benzylaniline–Antimony Tribromide.—The mixtures were dark green both in the liquid and the solid state.

The diagrams (Fig. 2) have three branches, showing the formation, in each system, of one stable compound only, having the composition $Ph{\cdot}CH_2{\cdot}NHPh,SbCl_3$ or $Ph{\cdot}CH_2{\cdot}NHPh,SbBr_3$.

FIG. 2.



Mols. of benzylaniline per 100.

I *Antimony trichloride–benzylaniline.* II *Antimony tribromide–benzylaniline.*

Benzylaniline differs from the other similar aromatic compounds investigated in showing a greatly reduced reactivity towards antimony halides. No satisfactory reason can at present be assigned for this. Data for such optical properties as molecular refractive power which might throw light on the problem are not available.

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NEWTON ABBOT, DEVON.

[*Received, November 25th*, 1924.]

LXXXI.—*The Cryoscopic Method for Adsorption.*

By HENRY LORIMER RICHARDSON and PHILIP WILFRID ROBERTSON.

THE adsorption of substances from solution has been investigated in the past only by methods involving filtration of the equilibrium mixture and subsequent estimation of the concentration of solute in the filtrate. There has been no general method for studying the adsorption of a variety of substances actually in the presence of charcoal in such a manner that increasing concentrations may readily be investigated.

Cryoscopy furnishes such a general method; it has been found that the adsorption of any substance soluble in the chosen solvent may be determined from its freezing-point depression curves, and that it is a simple matter to follow the rate of change of adsorption with concentration.

The solvent first chosen was water, in order that the accuracy of the method might be checked for a solute the adsorption of which could be determined by some quite independent method. Such a solute is acetic acid. The values for the adsorption ratio of acetic acid in charcoal and water (the ratio C_2/C_1), determined by the cryoscopic method at initial concentrations of $N/2$, $N/5$, and $N/10$, were 0·19, 0·44, and 0·85, whereas the corresponding values determined by the ordinary method of titration were 0·19, 0·44, and 0·86.

The Beckmann apparatus with magnetic stirrer was employed. Determinations were made with considerable care, and by adopting special precautions—notably the use of an intermediate cooling bath employing a cryohydric mixture—highly comparable results were obtained.

The water used as solvent was kept free from contamination by atmospheric carbon dioxide. The materials used as solutes were all scrupulously purified according to the best methods available in the literature. The charcoal was an acid-extracted animal charcoal of medium adsorptive strength, which was extracted by boiling water until neutral, and finally activated by heating to redness in a silica tube in a current of nitrogen. Its activity remained sensibly constant over the whole period of the operations, as was determined from time to time by the titration method with acetic acid.

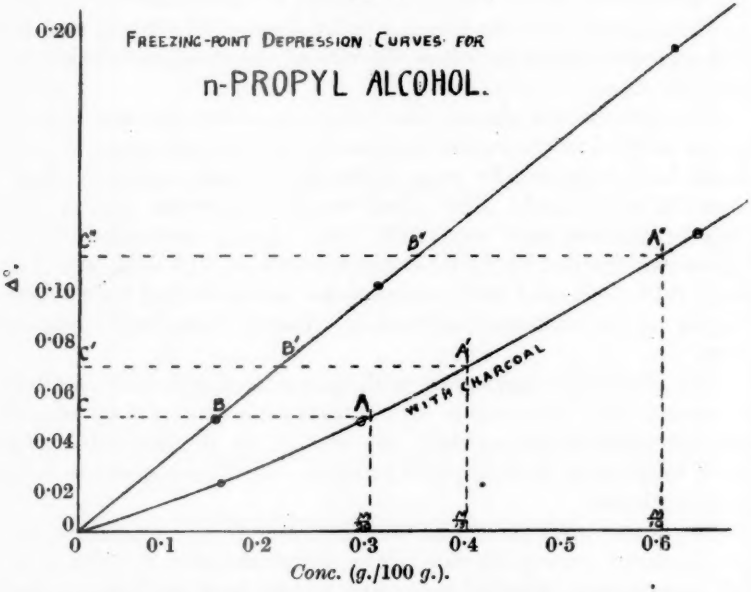
In order to show exactly the method of calculation, the values for one solute—*n*-propyl alcohol—may be given in detail. In these determinations, 25 g. of water were used, and 2·5 g. of charcoal; two series of observations were made with increasing concentration

of solute : one series in the absence of charcoal, the other with charcoal present.

Without Charcoal.			*With Charcoal.*		
G. of solute added.	Total conc. of solute (g./100 g.).	Depression.	G. of solute added.	Total conc. of solute (g./100 g.).	Depression.
0·0350	0·1400	0·046°	0·0366	0·1464	0·020°
0·0420	0·3080	0·101	0·0359	0·2900	0·045
0·0763	0·6132	0·199	0·0872	0·6388	0·123

In Fig. 1, the curves AA″ and BB″ represent the depressions obtained with and without charcoal, respectively; the vertical lines

FIG. 1.



correspond with concentrations of $M/20$, $M/15$, and $M/10$. The distances AB, A′B′, and A″B″ give the concentration of solute in the charcoal (C_2), and the distances BC, B′C′, and B″C′, the concentration in the solute (C_1), for initial concentrations of $M/20$, $M/15$, and $M/10$, respectively.

The logarithms of C_1/MW and C_2/MW for the compounds examined are plotted in Fig. 2; from these curves may be obtained the magnitude of n in the formula $C_2 = KC_1^{1/n}$ (which is substantially accurate at low concentrations).

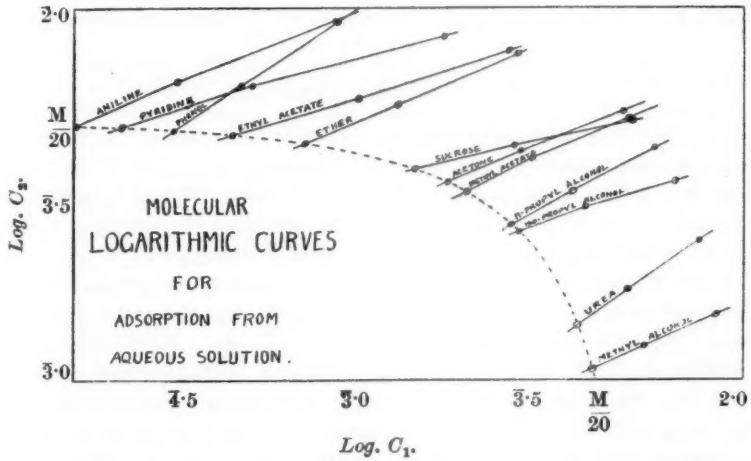
The following table summarises the results for the compounds examined, at an initial concentration of $M/20$; C_1 (in g. per 100 g.

of water) and C_2 (in g. per 10 g. of charcoal) were obtained from the freezing-point depression curves by the method given :

Substance.	C_1.	C_2.	C_2/C_1.	n.
Methyl alcohol	0·126	0·034	0·25	2·3
Carbamide	0·216	0·085	0·39	1·4
*iso*Propyl alcohol	0·150	0·151	0·95	3·6
n-Propyl alcohol	0·143	0·158	1·10	1·9
Methyl acetate	0·133	0·237	1·76	2·4
Acetone	0·093	0·197	2·12	2·6
Sucrose	0·450	1·262	2·79	4·8
Acetic acid (by titration)	0·0758	0·226	3·00	—
Ether	0·049	0·321	6·5	2·3
Ethyl acetate	0·0375	0·403	10·8	3·1
Phenol	0·028	0·443	15·9	1·5
Pyridine	0·017	0·378	22·5	3·8
Aniline	0·015	0·450	30·0	2·6

The magnitude of the ratio C_2/C_1 places the compounds in the order of the points on the dotted line in the diagram (Fig. 2);

FIG. 2.



C_2/C_1, therefore, gives a measure of the relative adsorbability of a compound for a given initial concentration. The "constant" K has no comparative significance, as it is dependent both on the concentration and on the index, n.

The magnitude of n lies, in the compounds examined, between 1·45 and 4·8, varying thus around the mean value of 3, which was obtained by Freundlich for substances of widely differing types in aqueous solution. There is, furthermore, no apparent connexion between the value of n and the relative adsorbability C_2/C_1; and the latter factor appears to depend only vaguely on constitutive influences. Aromatic compounds are more readily adsorbed than

aliphatic, and, generally, molecular complexity tends to increase the adsorbability of a compound.

The second substance chosen as solvent in the cryoscopic study of adsorption was phenol. With a sample of phenol rigorously purified and freed from water, measurements were carried out with the following solutes: methyl alcohol, stearic acid, methyl succinate, water, and benzene. In every instance, the adsorption was nil, even for a compound of some complexity such as stearic acid. This completely negative result is surprising, although in agreement with the generally recognised fact that compounds which are readily adsorbed, as solvents prevent adsorption.

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[*Received, January 24th*, 1925.]

LXXXII.—*Substitution in Resorcinol Derivatives. Part I. Nitration of Derivatives of β-Resorcylaldehyde.*

By MYSORE GURU SRINIVAS RAO, COLLURAYANA SRIKANTIA, and MYSORE SESHA IYENGAR.

THIS communication, which deals with the nitration of 2-hydroxy-4-methoxybenzaldehyde [4-methoxy-β-resorcylaldehyde *] (Srinivas Rao and Sesha Iyengar, *Perf. Essent. Oil Rec.*, 1923, **14**, 300) and its derivatives, is a contribution to the study of the position taken by an entering group in polysubstituted benzenes.

β-Resorcylaldehyde on nitration gives 5-nitro-β-resorcylaldehyde (Gattermann, *Annalen*, 1907, **357**, 313, 383) and the corresponding acid (Hemmelmeyer, *Monatsh.*, 1904, **21**, 45; 1905, **26**, 185). Perkin (J., 1902, **81**, 1056), while working with brazilin, showed that the nitro-acid isolated from his nitrated mother-liquors was identical with that obtained by nitrating *p*-methoxysalicylic acid; he stated that it "probably is 5-nitro-acid." Bauer (*Ber.*, 1915, **48**, 509) nitrated 2 : 4-dihydroxyphenylarsinic acid and 4-hydroxy-2-methoxyphenylarsinic acid and in both cases found the nitro-group in position 5. In the nitration of salicylaldehyde the 3- and

* Goulding and Pelly, who were the first to isolate this aldehyde from natural sources (P., 1908, **24**, 62; 1911, **27**, 235), have taken exception to one of our statements (*loc. cit.*) regarding its identity, as being "erroneous and misleading." The method by which they claim to have established the constitution of their new compound as 4-methoxy-β-resorcylaldehyde, *viz.*, by its conversion into β-resorcylic acid and resorcinol on fusion with potassium hydroxide (*Perf. Essent. Oil Rec.*, 1923, **14**, 370), cannot determine the position of the methoxy-group, for which, during the high-temperature reaction, a hydroxyl group was substituted.

the 5-nitro-aldehyde are both formed, the latter in the larger quantity (Mazzara, *Gazzetta*, 1876, **6**, 460).

In nearly all these cases the nitro-group entered position 5. In the light of the theory that substitution is usually preceded by addition, 2-hydroxy-4-methoxybenzaldehyde should yield on nitration either the 3- or the 5-nitro-acid; probably the latter, if steric influences affect the entry of the nitro-group into position 3. The results obtained by previous workers and by us are quite in accord with this conclusion. We obtained good yields of the 5-nitro-compounds in all cases, but, owing to the minute quantities of solids obtained from the nitration mother-liquors, we have not yet been able to decide if the 3-nitro-isomeride also is formed, and if a nitro-group is substituted for the aldehyde group (Salway, J., 1909, **95**, 1155; Harding, J., 1911, **99**, 1585).

In all cases where two specimens are stated to be identical, the identity was proved by direct comparison and by the determination of the m. p. of a mixture of the two.

Experimental.

5-Nitro-2-hydroxy-4-methoxybenzaldehyde was obtained as a red, crystalline substance by nitrating 2-hydroxy-4-methoxybenzaldehyde in glacial acetic acid solution at 10—15° for 6 hours (yield 75—80%); a further quantity of less pure material was precipitated on diluting the acetic acid mother-liquor. Purified by reprecipitation from dilute sodium hydroxide solution with dilute sulphuric acid, and dried in a steam-oven, the substance became almost white and melted at 168—169°. It crystallised from benzene in round nodules and from chloroform and alcohol in needles, decomposed carbonates, gave a red colour with ferric chloride, and did not reduce alkaline silver nitrate solution. In the Zeisel estimation, the expulsion of methyl iodide proceeded slowly and was not complete even after 2 hours (this was the case also with all the other nitro-compounds described here) (Found: N = 7·5; OMe = 15·12. Calc. for $C_8H_7O_5N$, N = 7·1; OMe = 15·74%).

The yellow oxime melts at 215—216°, and the orange phenylhydrazone at 197—198°.

5-Nitro-2-hydroxy-4-methoxybenzoic acid, m. p. 228° (decomp.), can be obtained by oxidising the nitro-aldehyde with permanganate or by nitrating *p*-methoxysalicylic acid (Perkin, *loc. cit.*). Heated (0·5 g. with 10 c.c. of water) in a sealed tube for about 5 hours at 160—170°, it was nearly quantitatively converted into 4-nitroresorcinol 3-methyl ether, m. p. 143° (Weselsky and Benedikt, *Monatsh.*, 1880, **1**, 887, give m. p. 144°) (Found: N = 8·5. Calc., N = 8·2%).

The nitro-group in the nitro-acid, and consequently in the nitro-aldehyde, is therefore in position 5. We tried to confirm this result by treating 5-nitro-β-resorcylic acid with methyl iodide and sulphate under different conditions, but methylation would not take place (compare Hemmelmeyer, *loc. cit.*), probably because of the presence of the *o*-nitro-group (compare Hewitt, Johnson, and Pope, J., 1913, **103**, 1628).

Methyl 5-Nitro-2-hydroxy-4-methoxybenzoate.—Methyl *p*-methoxysalicylate was prepared by gradually treating 10 g. of β-resorcylic acid, dissolved in sodium hydroxide solution (3 parts), with the calculated quantity of methyl sulphate. After 12 hours, the alkaline mixture was distilled with steam, and 2·5 g. of the ester were obtained. It had a pleasant smell, melted at 49°, and gave a violet-red colour with ferric chloride.

This ester (1 g.), dissolved in a little glacial acetic acid, was warmed with 1 c.c. of nitric acid (*d* 1·42), and as soon as a vigorous reaction set in the mixture was cooled. The crystals which separated were filtered, washed with acetic acid, and recrystallised from methyl alcohol. The pink crystals obtained melted at 137—138°, gave a red colour with ferric chloride, dissolved freely in glacial acetic acid, but were sparingly soluble in alcohols. The sodium derivative is less soluble than the potassium derivative.

This nitro-ester was boiled with alcoholic potash for 2 hours; addition of dilute sulphuric acid to the solution precipitated 5-nitro-2-hydroxy-4-methoxybenzoic acid. Since the nitro-group in this acid is in position 5, that in the nitro-ester also should be in the same position.

5-Nitro-2 : 4-dimethoxybenzaldehyde.—2 : 4-Dimethoxybenzaldehyde (2 g.; obtained from methyl sulphate, sodium hydroxide, and 2-hydroxy-4-methoxybenzaldehyde) was dissolved in 8 c.c. of glacial acetic acid, 3 c.c. of nitric acid (*d* 1·42) were added, and the mixture was left in cold water for 12 hours. The pink needles which had separated were washed with a little acetic acid and crystallised from methyl alcohol; m. p. 188—189° (yield 75—80%).

The same nitro-compound was obtained by methylating 5-nitro-2-hydroxy-4-methoxybenzaldehyde in chloroform solution with methyl iodide and silver oxide. The yield was equally good, the solid was yellow and melted a degree higher.

The light yellow oxime melts at 184—185°, and the hydrazone, orange plates, at 169—170°. The nitro-aldehyde is sparingly soluble in alcohols, gives no colour with ferric chloride, and is insoluble in cold alkalis. If, however, it is boiled with alkalis, it gradually dissolves and a yellow solid of indefinite m. p. is precipitated on addition of dilute sulphuric acid to the cooled solution.

4-Methoxy-2-ethoxybenzaldehyde was prepared by ethylating 2-hydroxy-4-methoxybenzaldehyde in chloroform solution with ethyl iodide and silver oxide. The crude yellow solid was dissolved in ether, and the unchanged phenolaldehyde extracted with dilute caustic soda solution. The white solid finally obtained, m. p. 65—66°, was easily soluble in alcohols, chloroform, or acetic acid, insoluble in alkalis, volatile with steam, gave no colour with ferric chloride, and did not reduce silver nitrate solution readily. The pearly-white oxime melted at 95—96°, and the hydrazone, yellow plates, at 110—111°.

5-Nitro-4-methoxy-2-ethoxybenzaldehyde, m. p. 136—137°, obtained by nitrating the preceding aldehyde in the same way as methyl *p*-methoxysalicylate (above), is sparingly soluble in alcohols and more so in acetic acid or chloroform (Found : N = 6·34. Calc. for $C_{10}H_{11}O_5N$, N = 6·22%).

The same compound, m. p. 138—139°, was prepared by ethylating 5-nitro-2-hydroxy-4-methoxybenzaldehyde in chloroform with ethyl iodide and silver oxide. It did not give any colour with ferric chloride. Its yellow oxime melted at 185—186°, and the yellow hydrazone at 185—186°.

The nitro-compounds obtained by alkylating nitro-phenolic aldehydes by Purdie's method are usually yellow and melt a degree higher than those obtained by direct nitration of the dialkyloxy-aldehydes. The latter are red or brown, and melt quite sharply; repeated crystallisation does not improve either the colour or the m. p.

Preliminary Note on the Behaviour of 2-Hydroxy-4-methoxybenzaldehyde.

This aldehyde, unlike its isomeride vanillin, is affected by moisture. It is converted by halogen acids (except hydrofluoric) into dark red solids, which are soluble in caustic alkalis and are reprecipitated by acids. The red substance produced by concentrated hydrochloric acid contains methoxy-groups but no halogen, and gives an acetyl derivative and a crimson bromo-derivative. Hot dilute phosphoric and sulphuric acids have no action on the aldehyde, but the cold concentrated acids slowly produce red solutions. On bromination in absence of sodium acetate, the aldehyde gives a red compound, probably formed by the action of the liberated hydrogen bromide.

2 : 4-Dimethoxy- and 4-methoxy-2-ethoxy-benzaldehyde are more soluble than 2-hydroxy-4-methoxybenzaldehyde in concentrated hydrochloric acid, and from the solutions violet and crimson amorphous solids are deposited.

Unlike the phenolic aldehydes and their ethers, the nitro-phenolic aldehydes and their ethers do not give coloured solids with hot concentrated hydrochloric acid.

There is no mention in the literature of this peculiar behaviour of these aldehydes, and it is being studied.

Like vanillin, 2-hydroxy-4-methoxybenzaldehyde may be used to detect traces of indole in cultures. Under equivalent conditions, it produces similar, but more delicate and less transient, colorations.

A New Indicator. Vanillylidenenitromethane.

This compound (Knoevenagel, *Ber.*, 1904, **37**, 4502) can be used for colorimetric measurements of p_H-concentration within two ranges, namely, $p_H = 7$ to 8·5 and $p_H = 10$ to 11·5, being especially sensitive within the latter. A rough determination, kindly made for us by Mr. B. Sanjiva Rao, gave: $p_H = 2$—6, pale yellow; $p_H = 7$, pale pink; $p_H = 8$—10, pink; $p_H = 11$, pale pink; and $p_H = 12$, colourless. It is sensitive to carbonic acid, but gives sharp results with ammonia and mineral acids.

The indicator may be prepared by dissolving vanillin in absolute alcohol and adding the calculated quantity of nitromethane and a little ammonium carbonate. The long, deep yellow needles which separate after 2 days are washed with a little dilute sulphuric acid and with water.

CENTRAL COLLEGE, BANGALORE. [*Received, September 29th*, 1924.]

LXXXIII.—*Syntheses of Substituted Succinic Acids containing Aromatic Residues.*

By WILSON BAKER and ARTHUR LAPWORTH.

THE method first used by Lapworth (P., 1904, **20**, 245) for the preparation of alkylsuccinic acids was worked out in detail by Lapworth and McRae (J., 1922, **121**, 1699) in the cases of phenyl- and piperonyl-succinic acids. Briefly, the method consisted in treating an aqueous solution of the sodium arylidenecyanoacetate, formed from the aldehyde and sodium cyanoacetate solution, with potassium cyanide, and hydrolysing the addition product to the substituted succinic acid, which, in the case of phenylsuccinic acid, was obtained in a yield of 65—70% calculated from the weight of benzaldehyde used.

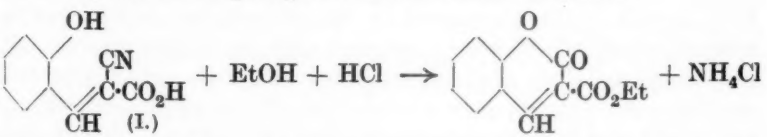
Higginbotham and Lapworth (J., 1922, **121**, 49) showed that the maximum additions of the elements of hydrogen cyanide to

αβ-ethylenic linkings were obtained by treating the carboxylic esters, rather than the acids, with excess of potassium cyanide. It was therefore expected that by using the esters of the arylidenecyanoacetic acids instead of their salts the addition of alkali cyanide would take place more readily and that better yields of the succinic acids would be obtained. This expectation has been fully realised, excellent yields of the succinic acids being obtained, except in those cases where specific difficulties of isolation of the acid (see vanillylsuccinic acid) or of hydrolysis of the addition product (see piperonylsuccinic acid) occurred.

Except in cases where an *o*-hydroxyl group is present, the arylidenecyanoacetic acids are completely esterified by boiling with alcohol containing a little anhydrous hydrogen chloride, and these esters readily react with sodium cyanide with evolution of heat, the products on hydrolysis giving the arylsuccinic acids. In the case of phenylsuccinic acid the yield from the benzaldehyde was 85% of the theoretical. In connexion with this preparation, it is interesting to note the influence which the α-cyano-group exerts on the reactivity of the double bond towards sodium cyanide; thus, whilst the above experiment indicated that the addition of sodium cyanide to benzylidenecyanoacetic ester must take place quantitatively and with great rapidity, since the yield of phenylsuccinic acid, calculated from the ester, was 95%, Higginbotham and Lapworth (*loc. cit.*) found that, in the case of cinnamic ester, the addition product gave on hydrolysis only a 20% yield of phenylsuccinic acid.

The attempted esterification of salicylidenecyanoacetic acid led to some interesting observations which have established the stereochemical formula of this acid, and possibly those of the arylidenecyanoacetic acids in general.

By boiling a solution of the acid in alcohol with a small amount of anhydrous hydrogen chloride, a bulky, white solid was first produced which slowly dissolved, giving a solution of ethyl coumarin-3-carboxylate and a precipitate of ammonium chloride :—



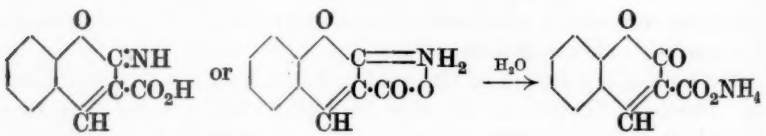
The insoluble solid consisted of free coumarin-3-carboxylic acid, either an imino-compound or ammonium coumarin-3-carboxylate, or perhaps both, and ammonium chloride.

It has been shown by several workers that salicylidenecyanoacetic acid is readily converted by the action of acids into coumarin-3-

carboxylic acid (see Haarmann and Reimer, D.R.-P. 189252). Bechert (*J. pr. Chem.*, 1894, [ii], **50**, 11) suggested that hydrolysis to salicylidenemalonic acid first took place, followed by lactone formation, but this view is untenable owing to the great stability of the nitrile group of the arylidenecyanoacetic acids (Lapworth and McRae, *loc. cit.*, p. 1702), which is entirely unaffected during the esterification of the carboxyl group, and also by prolonged boiling with concentrated hydrochloric acid.

The formation of coumarin-3-carboxylic acid is now shown to be a much more facile reaction than has hitherto been suspected. By bringing salicylidenecyanoacetic acid and water to the boiling point as quickly as possible, the yellow acid, itself insoluble in water, at once forms a colourless solution of ammonium coumarin-3-carboxylate, which, on cooling and acidifying, deposits the free acid, m. p. 187—188°, in theoretical yield. This reaction cannot be reconciled with Bechert's view, or with the view that lactone formation first takes place followed by hydrolysis of the 3-cyanocoumarin, since, although the case of hydrolysis of 3-cyanocoumarin is not recorded (see Bechert, *loc. cit.*), the corresponding amide, through which stage the hydrolysis would necessarily proceed, is entirely unaffected by many hours' boiling with water.

The authors hold that the only explanation of the reaction in accordance with the facts is that the cyano-group condenses with the *o*-hydroxyl group in the compound (I), forming an imino-compound (II), probably having the structure of an internal salt, which is immediately decomposed by water with formation of a solution of ammonium coumarin-3-carboxylate (III) :—



(II.) (III.)

This view is further supported by the observation that by boiling carefully dried salicylidenecyanoacetic acid with anhydrous alcohol, it is converted into a white, insoluble substance, which dissolves readily in cold water, giving a solution from which coumarin-3-carboxylic acid is thrown down on acidifying. This colourless compound must be the imino-compound or its internal salt, since the ammonium salt of the acid requires an additional molecule of water for its formation.

Hence, owing to the remarkable ease with which the cyano-group and the *o*-hydroxyl group interact, the acid must possess the

configuration in which these groups are adjacent, as shown in the formula (I).

This configuration, in accordance with the general nomenclature, is that of the "*trans*" acid, since the carboxyl and the hydroxyl group are not adjacent, and therefore do not form a lactone.

In contrast with the usual great stability of the nitrile groups of the arylidenecyanoacetic acids, Clarke and Francis (*Ber.*, 1911, **44**, 275) remark on the extraordinary ease with which the nitrile group of salicylidenecyanoacetic acid is hydrolysed with formation of coumarincarboxylic acid ("Cumarinsäure" is written instead of "Cumarincarbonsäure"). This apparently anomalous observation is at once explicable in the light of the above facts, since hydrolysis takes place, not of the cyano-group, but of the imino-group formed by its condensation with the *o*-hydroxyl group.

EXPERIMENTAL.

Esterification of the Arylidenecyanoacetic Acids.—The acids were all esterified under the same conditions, namely, by boiling the acid (25 g.) with alcohol (100 c.c.) containing anhydrous hydrogen chloride (3—4 g.) under reflux for 4 hours. The resulting solutions were filtered while hot and the esters crystallised out on cooling. The mother-liquors were concentrated and further small quantities obtained. The yields were all above 90% of those theoretically possible, and the esters were identical with those previously prepared from the aldehydes and ethyl cyanoacetate.

(1) *Phenylsuccinic Acid. Addition of Sodium Cyanide to Cyanophenylacrylic Ester.*—A mixture of cyanophenylacrylic ester (10 g.), alcohol (20 c.c.), and powdered sodium cyanide (5 g.) was gently heated on the steam-bath for 5 minutes, cooled, and water (200 c.c.) added. The resulting clear solution of the addition product was decomposed by hydrochloric acid, causing the precipitation of ethyl αβ-dicyano-β-phenylpropionate, $CHPh(CN)\cdot CH(CN)\cdot CO_2Et$, as a colourless oil, which, on standing, solidified to a mass of white crystals. (This compound, which has been described by Higson and Thorpe, J., 1906, **89**, 1471, may be recrystallised from dilute methyl alcohol and obtained as colourless prisms, m. p. 64°).

Hydrolysis of the dicyano-compound. The ethyl αβ-dicyano-β-phenylpropionate was hydrolysed by boiling with concentrated hydrochloric acid (40 c.c.) for 4 hours. The solution, on cooling, deposited phenylsuccinic acid in small, white crystals, m. p. 165°, and a further small amount was obtained from the mother-liquor. The yield was 95% of that theoretically possible from the ester used.

(2) *Vanillylsuccinic Acid.*—Vanillylidenecyanoacetic acid was

prepared by Lapworth and McRae's general method (*loc. cit.*) by condensing vanillin (20 g.), dissolved in 10% sodium hydroxide solution (200 c.c.), at 60° with a solution of sodium cyanoacetate.

Addition of sodium cyanide to cyanovanillylacrylic ester and hydrolysis of the product. A mixture of cyanovanillylacrylic ester (25 g.), water (200 c.c.), and sodium cyanide (12·5 g.) was warmed on the steam-bath for ½ hour, when the original, intensely orange-yellow colour vanished.* The solution was concentrated till it became viscous, and the addition product hydrolysed by boiling with strong hydrochloric acid (100 c.c.) for 18 hours. The resulting solution of vanillylsuccinic acid and ammonium chloride was evaporated to dryness, and the former extracted with hot acetone, the solvent distilled off, and the dark residue dissolved in hot water (25 c.c.). On standing, vanillylsuccinic acid separated; the crystals were washed with a very little ice-cold water. By working up the mother-liquor the crude acid was obtained in 45% yield calculated from the weight of the ester used. The yield was poor owing to the extreme solubility of the acid in water, and attempts to isolate that remaining in solution as the carbethoxy-derivative (see below) resulted in uncrystallisable oils. It was recrystallised from water, then dissolved in boiling ether, and the filtered solution evaporated to a small bulk, when the acid crystallised in small, colourless crystals, m. p. 175—176° (Found: C = 54·85; H = 5·16; equiv. = 119·3. $C_{11}H_{12}O_6$ requires C = 54·98; H = 5·04%; equiv. = 120·1).

Vanillylsuccinic acid is readily soluble in water, ethyl alcohol, or acetone; almost insoluble in benzene or chloroform. It dissolves in aqueous sodium hydroxide, giving at first a colourless solution, which usually in a few seconds turns yellow and gradually, during a couple of minutes, assumes a reddish-pink colour, which is destroyed on acidifying, but reappears on making alkaline. In a solution of sodium carbonate the same phenomenon is observed, but the colour is less intense. These colorations are due to oxidation and the presence of the *p*-hydroxyl group, since if either oxygen is excluded, or the hydroxyl group is protected, no colour is observed. In an aqueous solution of the acid a minute trace of ferric chloride produces a bluish-green colour, but with slightly more of the reagent the colour

* The stages of the reaction are readily observed by treating the ester (5 g.) with 50% alcohol (30 c.c.) and sodium cyanide (2·5 g.), when the at first intensely orange-yellow solution of the sodium salt,

$$NaO{\cdot}C_6H_3(OMe){\cdot}CH{:}C(CN){\cdot}CO_2Et,$$

slowly deposits crystals, until in about 15 minutes a semi-solid yellow mass of the salt results. During the course of several hours this becomes more and more fluid, giving finally a clear solution of the sodium cyanide addition product.

lasts for only a fraction of a second and a brown solution results. This also is probably an oxidation phenomenon.

The *carbethoxy* derivative was obtained by the interaction of chloroformic ester and the acid in alkaline solution. It was precipitated on the addition of acid and recrystallised from ethyl acetate, being obtained in colourless crystals, m. p. 197—198° (Found : C = 53·72; H = 5·25; equiv. = 155·8. $C_{14}H_{16}O_8$ requires C = 53·82; H = 5·17%; equiv. = 156·1). It is easily soluble in alcohol or acetone, sparingly soluble in ether or cold water. It dissolves in a solution of sodium hydroxide without the formation of a pink colour, so long as the carbethoxy-group remains unhydrolysed.

Acetovanillylsuccinic anhydride, $AcO{\cdot}C_6H_3(OMe){\cdot}\overset{\displaystyle CO\text{———}O}{\underset{\displaystyle\quad\quad\quad}{CH{\cdot}CH_2{\cdot}CO}}$, was formed by boiling vanillylsuccinic acid with acetyl chloride. The crude product was washed with dry ether and recrystallised from chloroform–ligroin. It formed bunches of long, colourless needles, m. p. 112—113° (Found : C = 58·91; H = 4·44. $C_{13}H_{12}O_6$ requires C = 59·06; H = 4·58%). Acetovanillylsuccinic anhydride is readily soluble in chloroform, sparingly soluble in ether, and insoluble in ligroin.

(3) *Anisylsuccinic Acid*, $MeO{\cdot}C_6H_4{\cdot}CH(CO_2H){\cdot}CH_2{\cdot}CO_2H$.—The hydrolysis of the addition product of sodium cyanide to cyanoanisylacrylic ester proved to be more difficult than in the previous cases, since under similar conditions of hydrolysis, or by hydrolysing with alkalis, undesirable tarry products were obtained. The method finally adopted, which gave quite satisfactory results, was to treat the dinitrile in ethereal solution with anhydrous hydrogen chloride in the presence of alcohol, whereby the cyano-groups were converted into the imino-ether hydrochloride groups, $-C(OEt){:}NH,HCl$. The resulting substance was decomposed by water and was hydrolysed to the succinic acid by boiling with strong hydrochloric acid.

Addition of sodium cyanide to cyanoanisylacrylic ester and hydrolysis of the product. Cyanoanisylacrylic ester (5 g.), 50% alcohol (20 c.c.), and sodium cyanide (2·5 g.) were heated together on the steam-bath for 10 minutes. The resulting solution was diluted with water, acidified by hydrochloric acid, and the oily dicyano-compound extracted with ether. The extracts were dried, evaporated to about 25 c.c., alcohol (2 c.c.) was added, and the solution saturated at 0° with dry hydrogen chloride. Orange crystals, probably of the hydrochloride of the imino-ether, separated. After standing for 48 hours, the whole was hydrolysed by boiling with concentrated hydrochloric acid (100 c.c.) for 24 hours, when, on cooling, crude

anisylsuccinic acid separated. This product could not be satisfactorily crystallised owing to the presence of a small amount of tarry material, so the whole was evaporated to complete dryness, and the solid residue repeatedly washed with ether in a Soxhlet's apparatus until the filtrate was colourless. The remaining anisylsuccinic acid was recrystallised from boiling water and obtained in colourless, glistening, crystalline plates, m. p. 194—195°. The yield was 70% of that theoretically possible calculating from the weight of the ester used (Found : C = 58·93; H = 5·29; equiv. = 111·8. $C_{11}H_{12}O_5$ requires C = 58·90; H = 5·40%; equiv. = 112·0).

Anisylsuccinic acid is readily soluble in methyl or ethyl alcohol or acetone; almost insoluble in boiling benzene, ligroin or chloroform, or in cold ether.

Anisylsuccinic anhydride was prepared and recrystallised in the same manner as acetovanillylsuccinic anhydride. It separated as colourless, nacreous plates, m. p. 90·5° (Found : C = 63·69; H = 4·87. $C_{11}H_{10}O_4$ requires C = 64·05; H = 4·89%). It is easily soluble in chloroform or benzene, very sparingly soluble in ether, and insoluble in ligroin.

(4) Piperonylsuccinic acid (Lapworth and McRae, *loc. cit.*) was prepared in a manner similar to that used in making anisylsuccinic acid, but the yield was poor owing to the production of tarry matter during hydrolysis. It was best recrystallised by dissolving it in a large bulk of boiling ether, and concentrating the solution, from which it separated in small, colourless crystals.

Piperonylsuccinic anhydride, obtained and recrystallised in the usual manner (see acetovanillylsuccinic anhydride above), formed irregular, colourless crystals, m. p. 96° (Found : C = 59·76; H = 3·73. $C_{11}H_8O_5$ requires C = 59·98; H = 3·66%). It is easily soluble in chloroform, very sparingly soluble in ether or benzene, and insoluble in ligroin.

Attempted Esterification of Salicylidenecyanoacetic Acid.—Since salicylsuccinic acid has been prepared by Bredt and Kallen (*Annalen*, 1896, **293**, 366) by hydrolysis of the product of interaction of coumarin and potassium cyanide, its preparation along similar lines to the above was not attempted, but it was of interest to ascertain whether salicylidenecyanoacetic acid could be esterified, since by condensing salicylaldehyde with ethyl cyanoacetate only the "bis" product, $OH{\cdot}C_6H_4{\cdot}CH[CH(CN){\cdot}CO_2Et]_2$, is obtained (Bechert, *J. pr. Chem.*, 1894, [ii], **50**, 11), and the same substance is also formed by the action of ethyl cyanoacetate on salicylhydramide (Beccari, *Atti R. Accad. Sci. Torino*, 1902, **37**, 137).

(a) *Preparation of ethyl coumarin-3-carboxylate.* Salicylidenecyanoacetic acid (5 g.) was boiled with alcohol (50 c.c.) containing

anhydrous hydrogen chloride (0·5 g.). After 1½ hours, the liquor was filled with a bulky, white solid, which gradually dissolved on further boiling, leaving a precipitate of ammonium chloride. The solution on standing deposited ethyl coumarin-3-carboxylate (3·6 g.) as colourless needles, m. p. 94°. This was identified by hydrolysis to the acid, m. p. 187—188°, and by comparison with a known specimen.

(b) *Formation of coumarin-3-carboxylic acid and its ammonium salt.* An experiment similar to the above was carried out, but the boiling was discontinued after 1½ hours. The white substance (2·7 g.) was filtered off and washed with cold alcohol. By treating with cold water, it largely dissolved, giving a solution which deposited much coumarin-3-carboxylic acid on acidifying. The residue insoluble in water was free coumarin-3-carboxylic acid, which, when recrystallised from dilute alcohol, melted at 187—188° (Found: C = 63·12; H = 3·33. $C_{10}H_6O_4$ requires C = 63·16; H = 3·18%).

THE UNIVERSITY, MANCHESTER. [*Received, December 11th*, 1924.]

LXXXIV.—*Ring-chain Tautomerism. Part XII. Derivatives of ββ-Dimethyl-α-ethylglutaric Acid.*

By GEORGE ARMAND ROBERT KON, LAURENCE FREDERICK SMITH, and JOCELYN FIELD THORPE.

THE work of Pandya and Thorpe (J., 1923, **123**, 2852) was undertaken with the object of studying the conditions of ring formation in derivatives of αββ-trimethylglutaric acid, which is to be regarded as the simplest member of the ββ-disubstituted acids having a substituent in the α-position; one of the objects of the research was also to settle the question of the type of tautomerism exhibited by the substance known as Balbiano's acid and, if possible, to prepare the latter synthetically. It was found, however, that there existed a marked tendency for halogen derivatives in this series to undergo fission under mild experimental conditions and to form monobasic acids of the acrylic series, and it was, therefore, impossible to prepare any substance having the properties of the acid obtained by Balbiano from camphoric acid. The great importance attached to the problem led us to investigate other α-substituted glutaric acids, and the α-ethyl acid, $CO_2H{\cdot}CHEt{\cdot}CMe_2{\cdot}CH_2{\cdot}CO_2H$, was chosen as the first for attack. This acid is readily obtainable by Kon and Thorpe's method (J., 1922, **121**, 1795).

It may at once be stated that the results now described emphasise Pandya and Thorpe's conclusions regarding the function of an

α-alkyl group in modifying the tendency to ring formation to which the complex is liable.

Thus, there appears to be but little tendency for the bromo-derivatives of the α-ethyl acid to pass into derivatives of caronic acid, although we have isolated a certain quantity of a lactone which doubtless contains a trimethylene ring (VII) (see p. 569); there is also no evidence of the existence of ring-chain tautomerism between a keto- and a hydroxy-ring-acid such as is observed in glutaric acids without an α-substituent.

On the other hand, there is a very strong tendency, shared by derivatives of trimethylglutaric acid, for the whole molecule to undergo disruption with the formation of ββ-dimethyl-α-ethylacrylic acid (II), *e.g.*, when the dibromo-acid (I) is treated with an alkaline hydroxide :

$$\text{(I.)}\ Me_2C\!<\!\begin{matrix}CEtBr\cdot CO_2H\\ CHBr\cdot CO_2H\end{matrix} \longrightarrow \text{(II.)}\ Me_2C{:}CEt\cdot CO_2H + CO_2H\cdot CO_2H.$$

The formation of the acrylic acid in place of the expected trimethylene derivative may perhaps be an indication that the fission of the molecule precedes the elimination of hydrogen bromide, which then takes place with the production of the unsaturated acid. This view is rendered more probable by our observation that α-substituted glutaric acids are somewhat easily attacked even before they are brominated; in the process of hydrolysis leading to their formation from the alkylated Guareschi compounds (Kon and Thorpe, *loc. cit.*) they undergo fission to some extent, the alkylated portion of the chain being eliminated in the form of propionic or butyric acid, $>C\!<\!\begin{matrix}CHR\cdot CO_2H\\ CH_2\cdot CO_2H\end{matrix}$.

Experiments were therefore made to discover under what conditions the α-ethyl acid suffered disruption, and it was found that treatment with concentrated potassium hydroxide for a short time is sufficient to produce considerable quantities of butyric acid and acetic acid. Boiling with 70% aqueous sulphuric acid produces a similar effect, butyric acid and small quantities of neutral substances being obtained. The cause of this remarkable change is at present still awaiting explanation, but is doubtless attributable to steric factors.

A feature of the α-ethyl acid is the fact that in spite of careful working it appears to be impossible to isolate any monobromo-derivative under the usual conditions of the Hell-Volhard method of bromination, although the lactonic acid (III) (see below) must be formed from such a derivative.

Apart from these special features, the behaviour of the substances

investigated follows closely that of the trimethyl series, and the new compounds obtained in the course of the research need only be briefly mentioned.

When the dibromination product was esterified with alcohol, an acid fraction was always isolated, amounting to 30%. This consisted almost entirely of a lactonic acid analogous to that obtained in the trimethyl series and doubtless possessing the formula (III);* this substance was accompanied by a very small quantity only of an oil containing bromine and probably consisting of the monobromo-acid ester.

The neutral fraction consists of the αγ-dibromo-ester, which, like many of its homologues, cannot be purified by distillation, as it is partly converted into the bromolactonic ester (IV) by loss of ethyl bromide.

(III.) $Me_2C<\begin{matrix}CEt(CO_2H)\cdot O\\ CH_2\text{———}CO\end{matrix}$ $Me_2C<\begin{matrix}CBrEt\text{——}CO\\ CH(CO_2H)\cdot O\end{matrix}$ or

$Me_2C<\begin{matrix}CEt(CO_2Et)-O\\ CHBr\text{———}CO\end{matrix}$ (IV.)

Hydrolysis of either the ester or the bromolactone with aqueous alkali causes fission as already mentioned, oxalic acid together with ββ-dimethyl-α-ethylacrylic acid being the products. A very small quantity of an acid melting at 208° and possessing the formula $C_9H_{12}O_4$ was also isolated, but we were unable to prepare a sufficient quantity to establish its constitution.

The action of 5*N*-methyl-alcoholic potassium hydroxide on the dibromo-ester leads to a hydroxy-lactone, m. p. 63°, having the formula V or VI, whereas the dibromo-acid (*cis* or *trans*) gives under the same conditions a lactonic acid, $C_9H_{12}O_4$, to which the constitution (VII) must be assigned, and which is quite similar to the compound isolated in the trimethyl series. Hydrolysis with 2*N*-sodium carbonate leads to an inseparable mixture of the two isomeric hydroxylactonic acids (V and VI); analysis and titration results confirm this conclusion.

(V.) $CMe_2<\begin{matrix}CEt(CO_2H)\cdot O\\ CH(OH)\text{——}CO\end{matrix}$ $CMe_2<\begin{matrix}CEt(OH)\text{——}CO\\ CH(CO_2H)\cdot O\end{matrix}$ (VI.)

$CMe_2<\begin{matrix}CEt\text{——}CO\\ C(CO_2H)-O\end{matrix}$ (VII.)

When the dibromination product was poured into anhydrous formic acid, a mixture of dibromo-acids was obtained which could be separated into two compounds by extraction with benzene, in which one proved to be sparingly soluble; when freed from its more

* The reasons for adopting this formula will be given in Part XIV.

soluble isomeride, it melted at 178° and was probably the *trans*-compound, whilst the second acid, to which the *cis*-configuration was assigned, melted at 145°. The action of hydrolysing agents on these acids was the same as on the dibromo-ester. If 80% aqueous formic acid was used in place of the anhydrous reagent, the solid isolated contained in addition to the dibromo-acids a considerable quantity of another substance, which melts at 154—155° and is the bromolactonic acid corresponding to the ester (IV); it gives the same products on hydrolysis with alkalis.

EXPERIMENTAL.

ββ-Dimethyl-α-ethylglutaric acid was prepared as described by Kon and Thorpe (*loc. cit.*), but it was found that the usual method of hydrolysis gave rather low yields, the acid being contaminated with butyric acid formed as the result of fission. Better results were obtained by boiling the imide for 3 hours with 60% acid (by volume), then diluting to 50%, and boiling for another 3 hours.

Fission of ββ-*Dimethyl-α-ethylglutaric Acid.*—The acid was boiled under reflux with an excess of 70% (by volume) sulphuric acid for 3 hours and distilled in steam; some 70% of unchanged initial material was recovered from the residue after steam distillation. The distillate, which smelt strongly of butyric acid, was extracted with ether, and the butyric acid removed by means of sodium carbonate and isolated as calcium salt. The ether extract on evaporation gave an oil, which partially solidified on keeping. The solid, on crystallisation from light petroleum, formed needles, m. p. 82°, probably consisting of a lactone, $C_7H_{12}O_2$ (Found: C = 65·30; H = 9·05. $C_7H_{12}O_2$ requires C = 65·61; H = 9·45%); it has not yet been investigated.

ββ-Dimethyl-α-ethylglutaric acid was heated with 8 times its weight of fused potassium hydroxide for 10 minutes. Water was then added and the acidified mixture distilled in steam. The distillate contained acetic and butyric acids, the latter being isolated as calcium salt (Found: Ca = 18·81. Calc., Ca = 18·73%). No unsaturated compounds appeared to be formed. About 70% of unchanged initial material was recovered.

Bromination of ββ-*Dimethyl-α-ethylglutaric Acid.*—The bromination was carried out exactly as described by Pandya and Thorpe (*loc. cit.*), thionyl chloride being used to form the acid chloride; the excess of this reagent was removed by warming under reduced pressure before the bromine was added.

Dibromination.—The neutral fraction, consisting of the ester of the acid I, decomposed on distillation; the analysis specimen was therefore purified by keeping in an evacuated desiccator for several

days and formed a viscous, yellow oil (Found: Br = 38·90. $C_{13}H_{22}O_4Br_2$ requires Br = 39·79%).

On distilling the oil under reduced pressure, it partially decomposed, the greater part of the distillate boiling at 184°/12 mm. and probably containing some of the bromolactonic ester IV together with unchanged dibromo-ester (Found: Br = 35·03%); a pure compound was not isolated from it.

The acid fraction, obtained in about 30% yield, deposited a large quantity of a bromine-free solid, whilst the residual oil still contained bromine (Found: Br = 19·65. $C_{11}H_{19}O_4Br_2$ requires Br = 27·07%) and probably consisted of impure monobromo-acid ester. The solid crystallised well from benzene–light petroleum (b. p. 60—80°), forming large, irregular crystals, m. p. 97°, and consisted of the lactone III [Found: C = 57·94; H = 7·71; equiv. (monobasic) = 189·5. $C_9H_{14}O_4$ requires C = 58·08; H = 7·53%; equiv. = 186].

cis- *and* trans-αγ-*Dibromo*-ββ-*dimethyl*-α-*ethylglutaric Acids* (I).—When the dibromo-acid chloride was poured into anhydrous formic acid (5 vols.) instead of alcohol, the solution slowly deposited a crystalline solid on evaporation. The solid was drained on a porous plate, purified by washing with cold benzene, and separated into two fractions by extraction with hot benzene. The insoluble portion crystallised from acetone–benzene in large, rhombic crystals, m. p. 178° (decomp.); it was assumed to be the *trans*-dibromo-acid by analogy with other acids of this series (Found: Br = 45·67. $C_9H_{14}O_4Br_2$ requires Br = 46·23%). The benzene solution was mixed with light petroleum (b. p. 60—80°), when a more soluble acid separated, which was doubtless the *cis*-dibromo-acid; after several crystallisations from benzene and petroleum, it formed irregular, crystalline aggregates, m. p. 145° (decomp.) (Found: Br = 46·47%).

The mother-liquors from which the dibromo-acids had been obtained yielded on further dilution with light petroleum a solid which, on repeated crystallisation from acetone and light petroleum, formed large, transparent, rhombic crystals, m. p. 154—155°, and consisted of the bromolactone (IV) (Found: Br = 30·02. $C_9H_{13}O_4Br$ requires Br = 30·16%). This compound was the principal product when the dibromo-acid chloride was poured into 80% formic acid instead of the anhydrous reagent.

Monobromination.—All attempts to monobrominate ββ-dimethyl-α-ethylglutaric acid led to mixtures of dibromo-derivatives with unbrominated material. The amount of acid fraction obtained was high—usually 50%—and this was similar to that obtained in the dibromination, consisting almost entirely of the lactone, m. p. 97°. On pouring the monobromination product into formic acid, a

mixture of the original acid with its dibromo-derivatives was obtained.

Hydrolysis of the Dibromo-derivatives.—Action of dilute sodium carbonate. The dibromo-ester (30 g.) was boiled with 200 c.c. of 10% aqueous sodium carbonate, until the oil had completely dissolved (6 hours). The solution was cooled, extracted with ether, acidified, and again extracted; the dried extract gave an oil on evaporation which did not solidify and was purified by keeping in a vacuum for a fortnight; analysis showed that it was probably a mixture of hydroxy-lactones (Found: C = 53·61; H = 6·80; equiv. = 183 and 104. $C_9H_{14}O_5$ requires C = 53·45; H = 6·95%; equiv. = 202 and 101). A similar mixture was obtained from the dibromo-acids and the bromo-lactone on boiling with sodium carbonate.

Action of aqueous potassium hydroxide. The dibromo-ester (17 g.) was added in a thin stream to a boiling solution of 50 g. of potassium hydroxide in 28 c.c. of water. After boiling for a further 5 minutes, the solution was cooled, diluted, extracted with ether, strongly acidified with hydrochloric acid, and again repeatedly extracted with ether. The extract gave, on drying and evaporating, an oily residue which deposited a small amount of solid. This was purified by washing with dry ether and recrystallised from hot water, being obtained in sparkling plates, m. p. 208° (decomp.); the quantity was only sufficient for analysis (C = 59·01; H = 6·93. $C_9H_{12}O_4$ requires C = 58·83; H = 6·58%).

A further large quantity of solid was obtained on treating the residual oil from the separation of the above substance with light petroleum (b. p. 40—60°) and evaporating the solution so obtained. The solid crystallised well from water, forming small, rhombic prisms, m. p. 49·5°, and consisting of *ββ-dimethyl-α-ethylacrylic acid* (II) [Found: C = 65·70; H = 9·23; equiv. = 130. $C_7H_{12}O_2$ (monobasic) requires C = 65·61; H = 9·44%; equiv. = 128]. Oxalic acid also was produced in this reaction and was identified in the usual way in the aqueous mother-liquor.

ββ-Dimethyl-α-ethylacrylic acid and oxalic acid were also obtained when weaker alkali was used or when the dibromo-acids or the bromolactone was hydrolysed with strong or dilute alkali; hydrolysis of the supposed monobromo-ester also gave the same products.

Action of 5N-methyl-alcoholic potassium hydroxide. The dibromo-ester (10 g.) was poured in a thin stream into 30 c.c. of the boiling reagent, and the mixture boiled for 15 minutes. On working up in the usual way, an oil was obtained which partly solidified on keeping. The solid was drained on a porous plate and formed plates, m. p. 63°, on crystallisation from benzene and light petroleum (b. p. 40—

60°); it was doubtless one of the hydroxy-lactones (V and VI) (Found: C = 53·86; H = 6·96; equiv. with cold barium hydroxide = 201. $C_9H_{14}O_5$ requires C = 53·45; H = 6·95%; equiv.=202 and 101). No other crystalline substance could be isolated from the syrup accompanying the above lactone.

When the bromo-lactone or the dibromo-acids were hydrolysed in the same way, the product was an oil, from which a solid gradually separated. This was drained and purified by crystallisation from benzene and light petroleum (b. p. 40—60°); it formed plates, m. p. 80°, and consisted of the bridged lactonic acid VII (Found: C = 59·23; H = 6·70; equiv.=190 and 91. $C_9H_{12}O_4$ requires C = 58·83; H = 6·58%; equiv.=184 and 92); about 30% of ββ-dimethyl-α-ethylacrylic acid was also isolated from the more soluble portion of the product.

We are indebted to the Chemical Society for a grant which has partly defrayed the cost of this investigation.

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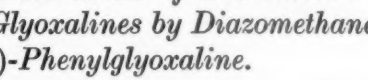
LXXXV.—*Tautomerism of Amidines. Part V. Methylation of Glyoxalines by Diazomethane. Bromination of 4(or 5)-Phenylglyoxaline.*

By WILLIAM GREENWOOD FORSYTH and FRANK LEE PYMAN.

THE results of methylating glyoxalines by methyl sulphate (J., 1924, **125**, 1431 and earlier) have now been supplemented by the use of diazomethane and of methyl sulphate in the presence of aqueous sodium hydroxide. They are as follows:

Methylation of 4(or 5)-R-Glyoxaline to:



Proportions of 5 : 1/4 : 1-isomeride.

	Me_2SO_4.	Me_2SO_4 + NaOH.	CH_2N_2.
R = NO_2	350 : 1 †	0·33 : 1	45 : 1
Br *	45 : 1	1 : 1 ‡	10 : 1
Ph	0·2 : 1 †	— §	0·5 : 1

* In 2 : 4(or 2 : 5)-dibromo-5(or 4)-methylglyoxaline.
† J., 1924, **125**, 1431. ‡ J., 1910, **97**, 1814.
§ 4(5)-Phenylglyoxaline is insoluble in aqueous sodium hydroxide.

In the cases of both the nitro- and bromo-compounds the 5 : 1-derivative is a stronger base than the 4 : 1-derivative, and it will

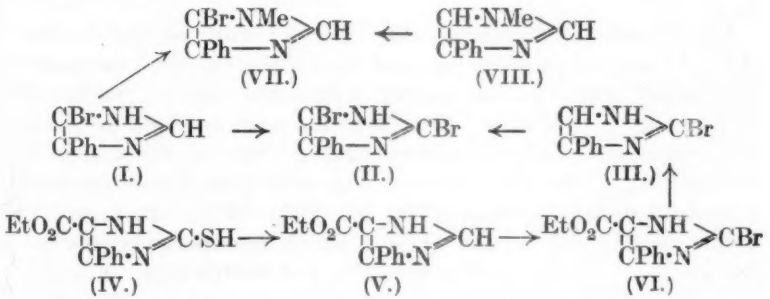
be observed that in these two cases the more basic compound is formed almost exclusively by the use of methyl sulphate alone, and greatly predominates with diazomethane, whereas methyl sulphate and alkali yield as much, or more, of the 4 : 1 as of the 5 : 1-isomerides. The results harmonise with those obtained by von Auwers and his collaborators (1919—1922) by the alkylation of indazoles. Here also the stronger bases—the 2-alkyl derivatives—are obtained, generally almost exclusively, by methyl iodide alone, whereas the same reagent in the presence of sodium methoxide yields, as a rule, mixtures of the 1- and 2-alkyl derivatives, whilst in the one case where diazomethane was used the 2-derivative was obtained exclusively. Moreover, the feebler bases result as the main products on distillation of 1 : 2-dimethylindazolinium iodides (von Auwers) or of 1 : 3-dimethyl-4(5)-nitro(or -bromo)glyoxalinium iodides (J., 1924, **125**, 1431, 1564).

4(5)-Bromo-5(4)-methylglyoxaline, which was previously found to yield with methyl sulphate and aqueous sodium hydroxide the two isomerides with Br : *N*Me as 5 : 1 and 4 : 1 in the proportions 3 : 2 (J., 1910, **97**, 1814), has now been found to yield the first of these almost exclusively, when methyl sulphate is employed alone. Similarly, 4(5)-*bromo*-5(4)-*phenylglyoxaline* (I) yields with methyl sulphate alone, almost exclusively the isomeride with Br : *N*Me as 5 : 1, the constitution of the product VII being shown by its formation from 4-phenyl-1-methylglyoxaline (VIII) (J., 1924, **125**, 1431) on bromination. These results are consistent with the previous observations that with methyl salts 4(or 5)-bromoglyoxaline yields the 5 : 1- and 4 : 1-Br : *N*Me derivatives in the proportions 34 : 1 (J., 1924, **125**, 1564), whilst the 4(or 5)-methyl (J., 1922, **121**, 2616) and 4(or 5)-phenyl (J., 1924, **125**, 1431) groups act in the opposite way, yielding respectively 2·2 and 4·8 times as much of the 4 : 1- as of the 5 : 1-isomeride.

4(5)-Bromo-5(4)-phenylglyoxaline was obtained as the main product together with 2 : 4(2 : 5)-*dibromo*-5(4)-*phenylglyoxaline* (II) by the action of 1 mol. of bromine in chloroform on 4-phenylglyoxaline, and its formation falls into line with the results of bromination of other 4(5)-substituted glyoxalines (Me, J., 1910, **97**, 1814; PhNH·CO, King and Murch, J., 1923, **123**, 621), where also the derivatives with a single 5(4)-bromo-substituent were isolated in quantity, whereas glyoxaline and its 1- and 2-methyl derivatives are converted into the fully brominated tri- or di-bromo-derivatives under similar conditions with mere traces of less fully brominated glyoxalines (J., 1922, **121**, 947, 2626; 1924, **125**, 1564). The constitution of 2 : 4(2 : 5)-dibromo-5(4)-phenylglyoxaline follows from the fact that it gives benzoic acid on

oxidation, and therefore contains both bromine atoms in the glyoxaline ring, whilst that of 5(4)-bromo-4(5)-phenylglyoxaline is deduced from the facts (1) that it yields the above dibromo-compound on bromination, and (2) that it is not identical with 2-*bromo*-4(5)-*phenylglyoxaline*) III, which was synthesised by a method similar to that employed for 2-bromo-4(5)-methylglyoxaline (J., 1923, **123**, 494).

The crude ethyl α-aminobenzoylacetate hydrochloride resulting from the reduction of ethyl *iso*nitrosobenzoylacetate was condensed with potassium thiocyanate, yielding *ethyl 2-thiol-4(5)-phenylglyoxaline-5(4)-carboxylate* (IV), which gave on oxidation *ethyl 4(5)-phenylglyoxaline-5(4)-carboxylate* (V). Treatment of this base with bromine in cold chloroform gave, besides unchanged material, a product which was not obtained in a pure state, but must have been crude ethyl 2-bromo-4(5)-phenylglyoxaline-5(4)-carboxylate (VI). This gave on hydrolysis and decarboxylation 2-bromo-4(5)-phenylglyoxaline (III), in which the attachment of the bromine to the glyoxaline nucleus was proved by bromination to 2 : 4(2 : 5)-dibromo-5(4)-phenylglyoxaline.



In the compounds I, II and III, the phenyl group exhibits a stabilising effect on the attachment of the bromine atoms (as also in 2-bromo-4 : 5-diphenylglyoxaline, J., 1924, **125**, 756), for these compounds are stable (or in the case of III fairly stable) towards 20% aqueous sodium sulphite at 100°, unlike the corresponding methylglyoxalines (J., 1923, **123**, 494), although they are reduced at higher temperatures.

EXPERIMENTAL.

Methylations by Methyl Sulphate.—2 : 5(2 : 4)-*Dibromo*-4(5)-*methylglyoxaline* (7·2 g.) and methyl sulphate (3·0 c.c.) reacted quickly when warmed; after the mixture had been heated for ½ hour in boiling water, aqueous sodium hydroxide was added and the mixture distilled with steam. The distillate gave on extraction

with ether 2 : 5-dibromo-1 : 4-dimethylglyoxaline (3·55 g., m. p. 41—43°, yield 55%),* and the residue gave on cooling 0·08 g. (yield 1·2%) of 2 : 4-dibromo-1 : 5-dimethylglyoxaline, m. p. 100—110°, which gave the pure substance on crystallisation from water, whilst the alkaline filtrate gave on treatment with hydrochloric acid and sodium carbonate 1·2 g. of 2 : 5(2 : 4)-dibromo-4(5)-methylglyoxaline, m. p. 212°.

5(4)-*Bromo*-4(5)-*methylglyoxaline* (10 g.) and methyl sulphate (6 c.c.) reacted immediately, the mixture being first cooled with water, and then heated in boiling water (10 mins.). After addition of aqueous sodium hydroxide (liquor L), ether removed an oil from which 5-bromo-1 : 4-dimethylglyoxaline was isolated as hydrogen oxalate (7·85 g., m. p. 96°, yield 55%), and in addition 1·8 g. of mixed bases were obtained. These were mixed with bromine (0·5 c.c.) in chloroform, and gave 2 : 5-dibromo-1 : 4-dimethylglyoxaline (1·1 g., m. p. 41·43°, yield 8%) and 2 : 4-dibromo-1 : 5-dimethylglyoxaline (0·01 g., m. p. 125°, yield 0·1%). The liquor L, when mixed with hydrochloric acid and sodium carbonate and extracted with ether, gave 1·85 g. of 5(4)-bromo-4(5)-methylglyoxaline, m. p. 153°.

5(4)-*Bromo*-4(5)-*phenylglyoxaline* (10 g.) and methyl sulphate (4·6 c.c.) reacted on warming, and after ½ hour at 100° the product was mixed with aqueous sodium hydroxide, when a white solid (8·5 g.) was precipitated. On extraction with hot light petroleum, 5(4)-bromo-4(5)-phenylglyoxaline (2·5 g., m. p. 228°) remained undissolved, whilst the extracted base gave pure 5-*bromo*-4-*phenyl*-1-*methylglyoxaline picrate* (11·42 g.; yield 73%). It forms fine, yellow needles, m. p. 226° (corr.), which are sparingly soluble in hot alcohol. (0·1315 gave 0·1984 CO_2 and 0·0319 H_2O. C = 41·2; H = 2·7. $C_{10}H_9N_2Br,C_6H_3O_7N_3$ requires C = 41·2; H = 2·5%). The same salt was isolated (yield 60%) from the product obtained by the action of bromine (1 mol.) in cold chloroform on 4-phenyl-1-methylglyoxaline. 5-*Bromo*-4-*phenyl*-1-*methylglyoxaline* crystallises from light petroleum in monoclinic prisms, m. p. 88—90° (corr.). (0·1095 gave 0·2025 CO_2 and 0·0389 H_2O. C = 50·4; H = 3·9. $C_{10}H_9N_2Br$ requires C = 50·6; H = 3·8%.)

Methylation by Methyl Sulphate and Sodium Hydroxide.—4(5)-*Nitroglyoxaline* (6 g.) in 10% aqueous sodium hydroxide (30 c.c.) was shaken with methyl sulphate (3 c.c.), cooling in water. A further 30 c.c. of aqueous sodium hydroxide and 3 c.c. of methyl sulphate were added, when 4-nitro-1-methylglyoxaline (2·3 g., m. p. 134°) separated; chloroform extracted a mixture from which

* In the experiments on methylation, yields are stated in percentages of the theoretical, allowing for recovered material.

0·65 g. of the same base, m. p. 134° (total yield 59%), was obtained after crystallisation from water. The filtrate from this gave 5-nitro-1-methylglyoxaline picrate (2·7 g., m. p. 153°, yield 19%), whilst the original alkaline liquor gave on acidification 1·0 g. of unchanged nitroglyoxaline.

Methylations by Diazomethane.—4(5)-*Nitroglyoxaline* (4·0 g.) was added to diazomethane in ether (50 c.c.) and washed down the condenser by methyl alcohol. Little obvious reaction took place, probably owing to the very sparing solubility of nitroglyoxaline in these solvents. After keeping over-night, no diazomethane remained, and the product gave 5-nitro-1-methylglyoxaline picrate (2·5 g., m. p. 153°, yield 58%), 4-nitro-1-methylglyoxaline (0·02 g., m. p. 134°, yield 1·3%), and recovered 4(5)-nitroglyoxaline (2·45 g.).

2 : 5(2 : 4)-*Dibromo*-4(5)-*methylglyoxaline* (8·0 g.) in methyl alcohol (40 c.c.) was added to diazomethane in ether (50 c.c.). Reaction took place immediately and after ½ hour no diazomethane remained. Separation of the products gave 2 : 5-dibromo-1 : 4-dimethylglyoxaline (1·5 g., m. p. 43°, yield 63%), 2 : 4-dibromo-1 : 5-dimethylglyoxaline (0·15 g., m. p. 126°, yield 6·3%), and recovered base (5·75 g., m. p. 215°).

4(5)-*Phenylglyoxaline* (10 g.) in methyl alcohol (50 c.c.) was added to diazomethane in ether (100 c.c.). Little reaction took place, and after 20 hours unchanged diazomethane was destroyed by the addition of acetic acid. Separation of the products gave 4-phenyl-1-methylglyoxaline picrate (3·8 g., m. p. 245°, yield 41%), 5-phenyl-1-methylglyoxaline picrate (1·85 g., m. p. 138—139°, yield 20%), and 4(5)-phenylglyoxaline nitrate (9·47 g., m. p. 174°).

Bromination of 4(5)-*Phenylglyoxaline.*—To 4(5)-phenylglyoxaline (20 g.) in chloroform (150 c.c.), one mol. of bromine (8 c.c.) in chloroform (40 c.c.) was added at 15° in ¾ hour. After removal of the solvent in a current of steam and addition of 500 c.c. of hot water, a mixture (A, 10·3 g.) separated. From the filtrate, sodium carbonate precipitated the monobromo-compound (17·5 g., m. p. 234°), whilst the mother-liquor, when acidified, concentrated, and mixed with sodium carbonate, gave 2·87 g. of 4(5)-phenylglyoxaline (m. p. 125°). Extraction of A with 5% aqueous sodium hydroxide left some monobromo-compound undissolved, and fractional precipitation of the solution with acid effected a partial separation of the mono- and di-bromo-compounds. After several repetitions of this treatment and crystallisation of the products from alcohol, there were obtained in the pure state 5(4)-bromo-4(5)-phenylglyoxaline (19·75 g., 64%) and 2 : 5(2 : 4)-dibromo-4(5)-phenylglyoxaline (4·56 g., 11%).

5(4)-*Bromo*-4(5)-*phenylglyoxaline* (I) crystallises from alcohol in

stout needles, melting at 242—245° (corr.) to a brown liquid. It is insoluble in water and sparingly soluble in cold organic solvents. It is insoluble in aqueous ammonia or sodium carbonate, and only soluble with difficulty in hot aqueous sodium hydroxide. (0·1850 gave 0·3277 CO_2 and 0·0540 H_2O. C = 48·3; H = 3·3. 0·1737 gave 18·7 c.c. N_2 at 17° and 761 mm. N = 12·7. 0·1495 gave 0·1258 AgBr. Br = 35·8. $C_9H_7N_2Br$ requires C = 48·4; H = 3·1; N = 12·6; Br = 35·9%).

The *hydrochloride* crystallises from 5*N*-hydrochloric acid in long, silky needles, which contain $2H_2O$. On treatment with water or on heating, it yields the base. (0·1972, air-dried, lost 0·0236 in a vacuum over sulphuric acid. Loss = 12·0. 0·1463, air-dried, lost 0·0363 at 120°. Loss = 24·8. $C_9H_7N_2Br,HCl,2H_2O$ requires $2H_2O$ = 12·2; $2H_2O + HCl$ = 24·5%).

The *nitrate* crystallises from dilute nitric acid in fine, pale yellow needles, m. p. 127° (corr.). It dissociates on the addition of water. (0·1061 gave 0·1484 CO_2 and 0·0275 H_2O. C = 38·2; H = 2·9. $C_9H_7N_2Br,HNO_3$ requires C = 37·8; H = 2·8%.)

The *picrate* separates from alcohol in bright yellow needles, m. p. 188—189° (corr.). (0·1140 gave 15·1 c.c. N_2 at 18° and 763 mm. N = 15·6. $C_9H_7N_2Br,C_6H_3O_7N_3$ requires N = 15·5%.)

The base crystallised partly in the free state from an alcoholic solution containing 1 mol. of oxalic acid.

Bromination.—5(4)-Bromo-4(5)-phenylglyoxaline, on treatment with bromine (1 mol.) in chloroform at 18—20°, gave 2 : 5(2 : 4)-dibromo-4(5)-phenylglyoxaline (m. p. 197—198°, alone or mixed; yield 78%) together with 18% of unchanged material.

Action of Sodium Sulphite.—(1) *At* 100°. 5(4)-Bromo-4(5)-phenylglyoxaline (1 g.) was boiled with sodium sulphite (2 mols.) in 20% aqueous solution for 6 hours and filtered hot, when 0·94 g. was recovered unchanged. (2) *At* 170°. The base (3 g.) was heated with sodium sulphite (2 mols.) in 20% aqueous solution for 3 hours at 170°. After addition of hot water, 0·76 g. of unchanged material (25%), m. p. 235°, was collected, whilst the mother-liquor deposited, on basifying and cooling, 1·1 g. of 4-phenylglyoxaline, m. p. 128°, and gave on extraction with chloroform a further 0·02 g., m. p. 126°, the total yield being thus 57% of the theoretical. Both substances were identified by the mixed-melting point method.

2 : 5(2 : 4)-*Dibromo*-4(5)-*phenylglyoxaline* (II) crystallises from aqueous alcohol in rectangular prisms, melting at 198—199° (corr.) to a brown liquid. It is insoluble in water, readily soluble in alcohol or acetone, and somewhat sparingly soluble in other cold organic solvents. It is soluble in aqueous solutions of ammonia, sodium carbonate or hydroxide, but insoluble in 5*N*-hydrochloric or

sulphuric acid. (0·2050 gave 0·2685 CO_2 and 0·0412 H_2O. C = 35·7; H = 2·3. 0·1795 gave 14·4 c.c. N_2 at 19° and 761 mm. N = 9·4. 0·1361 gave 0·1689 AgBr. Br = 52·8. $C_9H_6N_2Br_2$ requires C = 35·8; H = 2·0; N = 9·3; Br = 53·0%). On oxidation with alkaline permanganate, it gave benzoic acid (yield 65%; m. p. 110°), which was purified and identified by the mixed-melting point method.

Action of Sodium Sulphite.—(1) *At* 100°. After boiling for 3 hours with 1 mol., and for 6 hours with 2 mols., of 20% aqueous sodium sulphite, 2 : 5-dibromo-4-phenylglyoxaline was recovered unchanged to the extent of 93 and 76% respectively.

(2) *At* 130°. The base (3 g.) was heated for 3 hours with 2 mols. of sodium sulphite in 20% aqueous solution. The product was dissolved in aqueous sodium hydroxide, and acidified with hydrochloric acid, when 1·88 g. (63%) were recovered unchanged, m. p. 196—197°. The mother-liquor gave on the addition of sodium carbonate 0·07 g. of crude 5-bromo-4-phenylglyoxaline, m. p. 225° (3%), and after concentration 0·34 g. of 4-phenylglyoxaline, m. p. 128° (24%). The three substances were identified by the mixed-melting point method.

Ethyl 2-Thiol-4(5)-phenylglyoxaline-5(4)-carboxylate (IV).—Ethyl *iso*nitrosobenzoylacetate was obtained by a modification of Perkin's method (J., 1885, **47**, 244). To ethyl benzoylacetate (25 g.) in a little glacial acetic acid, sodium nitrite (10 g.) in saturated aqueous solution was added at 0°, when the *iso*nitroso-derivative separated (yield 97%) and gave 83% of the pure substance after crystallisation. This compound (10 g.) in 50 c.c. of alcohol was added slowly to 46 g. of hydrated stannous chloride in concentrated hydrochloric acid (100 c.c.) at 0°. The mixture was heated on the water-bath for ½ hour with 5 g. of tin foil, diluted with water, and freed from tin by means of hydrogen sulphide. After evaporation of the solvent under diminished pressure, there remained 7·7 g. of a greenish-white, semi-crystalline mass. This product, presumably the crude hydrochloride of ethyl α-aminobenzoylacetate, was dissolved in 20 c.c. of water, mixed with 5 g. of potassium thiocyanate in 10 c.c. of water, and heated in boiling water for 3 hours, when the thiol-ester separated; after crystallisation from alcohol, 4·8 g. were obtained in a pure state (40% of the theoretical yield, calculated on the *iso*nitroso-ester). The aqueous filtrate from the thiol-ester deposited some 2-thiol-4-phenylglyoxaline on concentration.

Ethyl 2-thiol-4(5)-phenylglyoxaline-5(4)-carboxylate crystallises from alcohol in plates, m. p. 219° (corr.). It is insoluble in water, slightly soluble in cold alcohol, but readily soluble in chloroform or hot alcohol. (0·1291 gave 0·2742 CO_2 and 0·0587 H_2O. C = 57·9; H = 5·1. $C_{12}H_{12}O_2N_2S$ requires C = 58·1; H = 4·8%).

Ethyl 4(5)-*Phenylglyoxaline*-5(4)-*carboxylate* (V).—The thiol-ester (4·72 g.) was added gradually to 70 c.c. of gently-boiling 10% nitric acid. When the effervescence had subsided, ammonia was added, when 3·68 g. of ethyl 4(5)-phenylglyoxaline-5(4)-carboxylate separated in a pure state (yield 89%). It crystallised from alcohol in needles, m. p. 225° (corr.). It is insoluble in water, and sparingly soluble in ether. (0·1267 gave 0·3080 CO_2 and 0·0041 H_2O. C = 66·3; H = 5·7. $C_{12}H_{12}O_2N_2$ requires C = 66·7; H = 5·6%).

Bromination Followed by Hydrolysis and Decarboxylation of the Crude Bromo-ester.—A suspension of 4 g. of ethyl 4(5)-phenylglyoxaline-5(4)-carboxylate in chloroform was mixed with 0·96 c.c. of bromine diluted with chloroform. After a short time the mixture was shaken with ammonia, when 1·08 g. of unchanged material (m. p. 219°) separated. The chloroform solution was evaporated, and the resulting oil was mixed with 30 c.c. of ether, when a further 0·42 g. (m. p. 211—220°) of unchanged material separated. The ethereal mother-liquor gave on evaporation 3·46 g. of crude bromo-ester as a light-brown gum. This substance (1·87 g.) was heated with 20 c.c. of 25% sulphuric acid for 3 hours at 170°. The product was basified with sodium carbonate and extracted with chloroform, when 1·05 g. of red gum were obtained. This was extracted with dry ether, which left the colouring matter mainly undissolved, and, on concentrating the solution, 0·52 g. of 2-bromo-4(5)-phenylglyoxaline crystallised in a pure state (yield 37% on the crude bromo-ester).

2-*Bromo*-4(5)-*phenylglyoxaline* (III) crystallises from ether in prisms, m. p. 153° (corr.). It is insoluble in water, and very easily soluble in alcohol, ether, or chloroform. It is soluble in dilute mineral acids or aqueous sodium hydroxide, but not in aqueous sodium carbonate or ammonia. (0·0966 gave 0·1732 CO_2 and 0·0304 H_2O. C = 48·9; H = 3·5; 0·1266 gave 0·1066 AgBr. Br = 35·8. $C_9H_7N_2Br$ requires C = 48·4; H = 3·1; Br = 35·9%.)

On treatment with bromine (1 mol.) in cold chloroform, it was converted into 2 : 5(2 : 4)-dibromo-4(5)-phenylglyoxaline (yield 96%, m. p. 196—197° alone or mixed).

Action of Sodium Sulphite.—(1) *At* 100°. 2-Bromo-4(5)-phenylglyoxaline (0·2 g.) was boiled with 2 mols. of sodium sulphite in 20% aqueous solution for 6 hours, and filtered hot from 0·14 g. of partly unchanged material, m. p. 135—145°. The m. p. was raised by the addition of 2-bromo-4(5)-phenylglyoxaline. The filtrate gave a little 4(5)-phenylglyoxaline picrate on the addition of aqueous picric acid. (2) *At* 150°. 2-Bromo-4(5)-phenylglyoxaline (0·2 g.) was heated with 5 mols. of sodium sulphite in 20% aqueous solution for 3 hours at 150°. The product was extracted with chloroform,

and the chloroform residue mixed with a hot aqueous solution of 0·24 g. of picric acid, when 0·29 g. (yield 86%) of 4(5)-phenylglyoxaline picrate separated; m. p. 212° (uncorr.) alone or mixed with an authentic specimen.

We desire to thank the Council of the Lord Kitchener National Memorial Fund for the grant of a scholarship which has enabled one of us (W. G. F.) to take part in the investigation.

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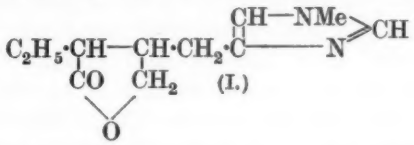
LXXXVI.—*The Relation of Pilocarpidine to Pilocarpine. Synthesis of* 1 : 4- *and* 1 : 5-*Dimethylglyoxalines.*

By RICHARD BURTLES, FRANK LEE PYMAN, and JAMES ROYLANCE.

HARNACK'S suggestion (*Annalen*, 1887, **238**, 228) that pilocarpidine is the imino-compound corresponding to pilocarpine is now proved to be correct by its conversion by methylation into a mixture of pilocarpine and an isomeric base, neo*pilocarpine* (I). Since pilocarpine is stereoisomeric with *iso*pilocarpine (Jowett, J., 1905, **87**, 794) and the latter yields on distillation with soda-lime 1 : 5-dimethylglyoxaline, and therefore contains the homopilopic complex in the 5-position with respect to the 1-methyl group, it is obvious that *neo*pilocarpine is the structural isomeride of pilocarpine



(I.)

containing the homopilopic complex in the 4-position with respect to the 1-methyl group. Like pilocarpine, *neo*pilocarpine is partially racemised by alkali with the formation of a stereoisomeric base, isoneo*pilocarpine*. Dr. J. H. Burn of the National Institute for Medical Research kindly tested *neo*pilocarpine, and reports that it has a very weak stimulating action on isolated intestinal muscle, but no perceptible trace of true pilocarpine action. In an anæsthetised cat, 100 mg., injected intravenously, caused a slight rise of arterial blood pressure, with no trace of inhibition of the heart's action, or of salivary secretion, whereas 0·1 mg. of pilocarpine, given subsequently, produced both these effects in typical form.

The identity of the dimethylglyoxaline obtained by the degrada-

tion of *iso*pilocarpine as the 1 : 5-isomeride was proved earlier (J., 1922, **121**, 2616) by an analytical method. The results have now been supplemented by the synthesis of this base (IV) by the oxidation of 2-*thiol*-1 : 5-*dimethylglyoxaline* (III), prepared in good yield by the condensation of *α-methylaminopropionacetal* (II) with thiocyanic acid—an obvious extension of the Wohl-Marckwald method to a secondary amino-acetal.

(II.) $(EtO)_2CH{\cdot}CHMe{\cdot}NHMe + HCNS \longrightarrow$

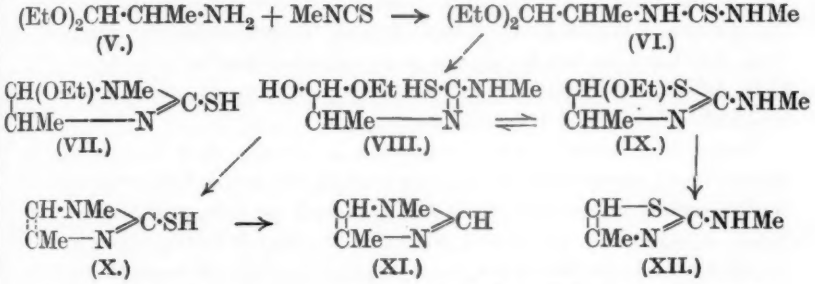
(III.) $\begin{matrix} CMe{-}NMe \\ \| \quad \quad > \\ CH{-}\!-\!-N \end{matrix} C{\cdot}SH \longrightarrow \begin{matrix} CMe{-}NMe \\ \| \quad \quad > \\ CH{-}\!-\!-N \end{matrix} CH$ (IV.)

The isomeric 1 : 4-dimethylglyoxaline (XI) has also been synthesised by the oxidation of 2-*thiol*-1 : 4-*dimethylglyoxaline* (X), but the formation of the latter compound did not proceed so smoothly as was expected. Whereas Wohl and Marckwald (*Ber.*, 1889, **22**, 568, 1354; 1892, **25**, 2355) have shown that acetalyl alkyl (or aryl) thiocarbamides of the general formula $(OEt)_2CH{\cdot}CH_2{\cdot}NH{\cdot}CS{\cdot}NHR$ readily yield on short hydrolysis with dilute mineral acids 2-thiol-1-alkyl (or aryl) glyoxalines, the condensation product of *α-aminopropionacetal* (V) and methylthiocarbimide—doubtless α-propionacetalylmethylthiocarbamide (VI)—gave only 8% of 2-thiol-1 : 4-dimethylglyoxaline, the main product being a base, $C_7H_{14}ON_2S$, which is slowly converted into 2-thiol-1 : 4-dimethylglyoxaline on boiling with dilute mineral acids, but yields, besides this compound and its *S*-ethyl ether,* 2-methylamino-4-methylthiazole (XII) when heated at 150° with concentrated hydrochloric acid. The latter base was prepared for comparison by the action of chloroacetone upon methylthiocarbamide, a method previously employed by Traumann (*Annalen*, 1888, **249**, 31) and Young and Crookes (J., 1906, **89**, 59), neither of whom obtained it in a pure state.

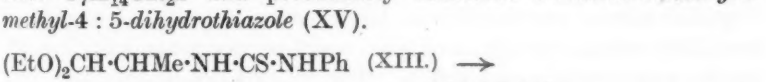
Now towards hydrochloric acid at 150°, 2-thiol-1 : 4-dimethylglyoxaline is quite stable, and 2-methylamino-4-methylthiazole, although not recoverable wholly unchanged, is not converted into 2-thiol-1 : 4-dimethylglyoxaline. Both compounds therefore arise by the removal of a molecule of alcohol from the base $C_7H_{14}ON_2S$. Of the two formulæ VII and IX for this base, only the second represents a compound which would be expected to have more than feeble basic properties, and it thus appears that this substance is 2-*methylamino*-5-*ethoxy*-4-*methyl*-4 : 5-*dihydrothiazole* (IX). With the adoption of this formula, the varying results of hydrolysis may be readily deduced from the knowledge that half-acetals are readily hydrolysed by hot dilute mineral acids, whereas the de-ethoxylation

* The ease of formation of this substance from the thiol compound is remarkable (compare p. 588).

of the ethoxy-derivatives of cyclic compounds requires the use of strong acids at high temperatures. Here strong hydrochloric acid at 150° converts the substance (partly) into XII, doubtless by way of the 5-hydroxy-4 : 5-dihydro-compound, whilst dilute mineral acids at lower temperatures are unable to effect the direct de-ethoxylation of (IX), but convert it into (X), presumably by fission of the nucleus and hydrolysis leading first to the half-acetal (VIII), and then to the corresponding aldehyde, which yields (X) by internal condensation.



It was found that *α-propionacetalylphenylthiocarbamide* (XIII) gave on short hydrolysis with dilute mineral acids only 28% of *2-thiol-1-phenyl-4-methylglyoxaline* (XIV), the main product of the reaction being a base, $C_{12}H_{16}ON_2S$, of similar character to the base $C_7H_{14}ON_2S$ and presumably therefore *2-anilino-5-ethoxy-4-methyl-4 : 5-dihydrothiazole* (XV).



These facts led us to reinvestigate the behaviour of acetalylphenylthiocarbamide. Wohl and Marckwald found that whilst hot 30% sulphuric acid converted this substance into 2-thiol-1-phenylglyoxaline, cold concentrated sulphuric acid transformed it into a base, $C_{11}H_{16}O_2N_2S$, which gave a picrate and chloroplatinate derived from the anhydro-form, $C_{11}H_{14}ON_2S$, to which they attributed the formula XVI or XVII, since it gave 2-thiol-1-phenyl-

glyoxaline on hydrolysis with dilute sulphuric acid. We find that the free base has the formula $C_{11}H_{14}ON_2S$ as in the salts, that it is also formed to a slight extent, together with 2-thiol-1-phenylglyoxaline, on hydrolysis of the thiocarbamide with dilute sulphuric acid, and that it yields with hydrochloric acid at 150° not only

2-thiol- and 2-*ethylthiol*-1-*phenylglyoxalines*, but also a small proportion of 2-anilinothiazole. It is clearly of similar character to the base $C_7H_{14}ON_2S$ and would thus appear to be 2-anilino-5-ethoxy-4 : 5-dihydrothiazole. One other similar case is recorded by Marckwald (*Ber.*, 1892, **25**, 2355), who states that acetalyl-*m*-xylylthiocarbamide yields on treatment with strong sulphuric acid a crystalline base, $C_{13}H_{20}O_2N_2S$, giving a picrate,

$$C_{13}H_{18}ON_2S,C_6H_3O_7N_3.$$

We repeated this experiment and obtained the picrate, but did not obtain the base in a crystalline condition, either directly or through the picrate. We were therefore unable to determine its composition, but have no doubt that it is constituted similarly to the base $C_7H_{14}ON_2S$, and that, if his analyses are correct, it contains a molecule of water of crystallisation.

From these results, the conclusion is drawn that the primary products of hydrolysis of acetalyl alkyl (or aryl) thiocarbamides with aqueous mineral acids at 100° are half-acetals, and that these form equilibrium mixtures with their anhydro-derivatives—the 5-ethoxy-4 : 5-dihydro-2-alkyl (or aryl)aminothiazoles—and water, the condition of equilibrium being determined by the substituents present.

EXPERIMENTAL.

Methylation of Pilocarpidine.—The base from 15 g. of pure pilocarpidine nitrate was mixed with 15 c.c. of methyl iodide. Reaction took place spontaneously, and was completed by heating for 1 hour on the water-bath under reflux. The bases were regenerated and converted into nitrates. On then adding ammonia and silver nitrate, unchanged pilocarpidine was precipitated as the silver salt, whilst chloroform extracted the tertiary bases from the filtrate. They were converted into nitrates and crystallised from absolute alcohol, when pilocarpine nitrate (1·8 g.) separated. The bases regenerated from the mother-liquors were converted into hydrochlorides, and the solution was evaporated to a syrup and mixed with acetone, when *neo*pilocarpine hydrochloride (2·1 g.) separated. Repetition of these operations gave a further 0·15 g. of each salt, whilst the remaining mixture of tertiary bases amounted to only 0·4 g. The crude pilocarpine nitrate melted at 173° and after crystallisation from alcohol melted at 178° (corr.), alone or mixed with an authentic specimen, and had $[\alpha]_D + 80°$ ($c = 3·9$ in water). To confirm its identification the picrate was prepared; it melted at 159—160° (corr.), alone or mixed with an authentic specimen. Petit and Polonowski (*J. Pharm.*, **1897**, **5**, 430) give its m. p. as 159—160°, Jowett (J., 1900, **77**, 494) as 147°, but Dr. Jowett, who

kindly repeated its preparation—at the author's request—has since found the m. p. 161—162°.

neo*Pilocarpine hydrochloride* crystallises in large prisms on addition of acetone to its concentrated aqueous or alcoholic solution. It melts at 177° (corr.) and is deliquescent, and very easily soluble in water or alcohol. 0·1270 gave 0·2500 CO_2 and 0·0800 H_2O. C = 53·7; H = 7·1. 0·1696 gave 0·0994 AgCl. Cl = 14·5. $C_{11}H_{16}O_2N_2,HCl$ requires C = 54·0; H = 7·0; Cl = 14·5%. In aqueous solution (c = 4·116) it had $[\alpha]_D$ + 66·4°.

The *base* melts at 39—40° (corr.) and is readily soluble in water or organic solvents except light petroleum. The *nitrate* crystallises from absolute alcohol in rosettes of fine needles, m. p. 94—95° (corr.). It is not deliquescent, but is easily soluble in water or hot alcohol. The *picrate* crystallises from alcohol in fine needles, m. p. 117—119° (corr.).

isoneo*Pilocarpine* was prepared by boiling 0·7 g. of *neo*pilocarpine with 1 g. of potassium hydroxide in 1 c.c. of water and 10 c.c. of alcohol for 2 hours under reflux, and isolated as *picrate*, which formed yellow, prismatic needles, from alcohol, m. p. 125—126° (corr.). 0·1211 gave 0·2076 CO_2 and 0·0503 H_2O. C = 46·8; H = 4·7. $C_{11}H_{16}O_2N_2,C_6H_3O_7N_3$ requires C = 46·7; H = 4·3%. The *nitrate* crystallised from absolute alcohol in prisms, m. p. 105—106° (corr.), which were not deliquescent. The hydrochloride was not obtained in crystalline form.

α-*Bromopropionacetal* was obtained as an oil (b. p. 74—75°/16—17 mm.) by Stoermer (*Annalen*, 1900, **312**, 271), following Kraus (*Diss.*, Berlin, 1895), in a yield of 36% of the theoretical by a method not described in detail but similar to that used for the preparation of bromoacetal (yield 31% of the theoretical) by Fischer and Landsteiner (*Ber.*, 1892, **25**, 2549). By using dry ether as a diluent in the later stages of the bromination and eventually extracting the product completely with ether, the yield may be improved. Under these conditions, propionacetal (100 g., b. p. 121—125°) and calcium carbonate (40 g.) treated with bromine (126 g.) below 5° gave α-bromopropionacetal (87·6 g., b. p. 69°/14 mm. Yield 54%). (Found: Br = 37·7. Calc., Br = 37·9%).

α-*Aminopropionacetal* (V).—The *dl*-form has not been described in accessible literature, although it seems to have been made by Kraus (*loc. cit.*); compare Wohl (*Ber.*, 1908, **41**, 3599). Ammonia (56 g.) was passed into 95% alcohol (250 g.) at 0°, 31 g. of α-bromopropionacetal were added, and the mixture was heated for 12 hours at 125—130° in a steel autoclave. After distilling off the alcohol and ammonia, adding a little water, and extracting with ether, potassium carbonate was added, and the mixture extracted with

chloroform. This extract gave on distillation 9·8 g. of α-aminopropionacetal, boiling at 79—80°/40 mm. (yield 46%). It is a colourless liquid miscible with water, alcohol or chloroform, but less soluble in ether. 0·1001 gave 0·2074 CO_2 and 0·1037 H_2O. C = 56·5; H = 11·6. 0·1621 gave, by Kjeldahl's method, 0·0192 NH_3. N = 9·8. $C_7H_{17}O_2N$ requires C = 57·1; H = 11·6; N = 9·5%.

α-*Methylaminopropionacetal* (II) was prepared similarly from the product obtained by heating anhydrous methylamine (47 g.) in absolute alcohol (45 g.) with α-bromopropionacetal (47 g.) for 10 hours at 125—130°, when 18 g. (yield 50%) were obtained as a colourless oil, b. p. 66—69°/16—18 mm., and having similar solubilities to the previous compound. 0·0974 gave 0·2111 CO_2 and 0·1013 H_2O. C = 59·6; H = 11·6. 0·0742 gave by Kjeldahl's method, 0·0078 NH_3. N = 8·7. $C_8H_{19}O_2N$ requires C = 59·6; H = 11·8; N = 8·7%. Poorer yields of this compound were obtained by decreasing the time of reaction, the concentration of methylamine or its quantity relative to that of the acetal, or by increasing the temperature.

Condensation with Thiocyanic Acid.—α-Methylaminopropionacetal (2 g.) was added to a mixture of potassium thiocyanate (1·3 g. in 6 c.c. of water) and hydrochloric acid (1·2 c.c of conc. acid). After heating for 1 hour on the water-bath, another 0·5 c.c. of hydrochloric acid was added, and the liquid was concentrated on the water-bath, when 2-thiol-1 : 5-dimethylglyoxaline separated (1·45 g., pure, yield 91%). After adding sodium hydroxide to the mother-liquor, nothing was extracted by ether.

2-*Thiol*-1 : 5-*dimethylglyoxaline* (III) crystallises from water in colourless prisms, m. p. 261—262° (corr.) to a deep red liquid. It is very sparingly soluble in cold water, but readily soluble in boiling water, sparingly soluble in cold alcohol, and insoluble in ether. It dissolves readily in aqueous sodium hydroxide, and slowly in 5*N*-hydrochloric acid, but is insoluble in aqueous sodium carbonate or ammonia. 0·1025 gave 0·1754 CO_2 and 0·0579 H_2O. C = 46·7; H = 6·3. 0·1378 gave, by Kjeldahl's method, 0·0357 NH_3. N = 21·3. 0·1497 gave 0·2770 $BaSO_4$. S = 25·4. $C_5H_8N_2S$ requires C = 46·9; H = 6·3; N = 21·9; S = 25·0%. On oxidation with hot 10% nitric acid it gave 1 : 5-dimethylglyoxaline (yield 67%), which was isolated as picrate, m. p. 167—168° (corr.) alone or mixed with an authentic specimen, and further identified as chloroaurate, decomp. 218—219° (corr.) (Found : Au = 45·2. Calc., Au = 45·0%).

Condensation of α-Aminopropionacetal with Methylthiocarbimide.—A. α-Aminopropionacetal (7·7 g.) and methylthiocarbimide (3·9 g.) were mixed, when heat was developed. The product, which did

not crystallise on keeping over-night, was boiled with 20 c.c. of 5*N*-hydrochloric acid for 20 minutes under reflux. The solution was evaporated to a syrup, mixed with an excess of sodium hydroxide, and extracted with ether, which removed 8·5 g. of yellow oil. The alkaline mother-liquor deposited on acidification 2-thiol-1 : 4-dimethylglyoxaline (0·51 g., m. p. 209°), and after concentration a further 0·05 g., m. p. 204° (yield 8·4%). The yellow oil was added to 11 g. of picric acid in 100 c.c. of hot alcohol, when 15·0 g. of 2-methylamino-5-ethoxy-4-methyl-4 : 5-dihydrothiazole picrate, m. p. 157—158°, separated on cooling (yield 71%).

B. The condensation product of α-aminopropionacetal and methylthiocarbimide gave, after boiling under reflux for 6 and 16 hours, respectively, with hydrochloric acid (5 c.c. of 5*N*-acid per g.), 2-thiol-1 : 4-dimethylglyoxaline (pure, yields 40 and 32%), 2-methylamino-5-ethoxy-4-methyl-4 : 5-dihydrothiazole (yields of pure picrate 14 and 2%), and 2-ethylthiol-1 : 4-dimethylglyoxaline (yields of picrate, m. p. *ca.* 101°, 18 and 40%).

2-Thiol-1 : 4-dimethylglyoxaline (X) crystallises from water in colourless, elongated prisms, m. p. 211—212° (corr.) to a deep red liquid. It is sparingly soluble in cold water, readily soluble in 5*N*-hydrochloric acid or aqueous sodium hydroxide, but insoluble in aqueous sodium carbonate or ammonia. It is sparingly soluble in alcohol and very sparingly soluble in ether. 0·1022 gave 0·1752 CO_2 and 0·0602 H_2O. C = 46·8; H = 6·6. $C_5H_8N_2S$ requires C = 46·9; H = 6·3%. It was recovered unchanged after being heated with hydrochloric acid (5 c.c. of conc. acid to 1 g.) for 3 hours at 150°. On oxidation with hot dilute nitric acid, it gave 1 : 4-dimethylglyoxaline (yield 50%), which was isolated and identified as the picrate, which melted, alone or mixed with an authentic specimen, at 167—168° (corr.).

2-Methylamino-5-ethoxy-4-methyl-4 : 5-dihydrothiazole (IX) was recovered from the picrate, through the hydrochloride, as a colourless oil, which solidified slowly and then melted at 52° (corr.). 0·0868 gave 0·1524 CO_2 and 0·0642 H_2O. C = 47·9; H = 8·3. $C_7H_{14}ON_2S$ requires C = 48·3; H = 8·0%. It is insoluble in water, but very easily soluble in the usual organic solvents except light petroleum. The hydrochloride, hydriodide, and nitrate were not obtained in crystalline form. The *picrate* crystallised from alcohol in yellow needles, m. p. 158° (corr.). 0·1253 gave 0·1768 CO_2 and 0·0508 H_2O. C = 38·5; H = 4·5. 0·1705 gave 0·1013 $BaSO_4$. S = 8·2. $C_7H_{14}ON_2S,C_6H_3O_7N_3$ requires C = 38·7; H = 4·2; S = 7·9%. The *chloroplatinate* crystallised in yellow-brown scales, m. p. 201° (corr.; decomp.) on mixing cold concentrated solutions of platinic chloride and the hydrochloride. It was

decomposed by heating its aqueous solution and was therefore not recrystallised. 0·1470 gave 0·0372 Pt. Pt = 25·3.

$(C_7H_{14}ON_2S)_2,H_2PtCl_6$

requires Pt = 25·7%.

Hydrolysis of IX.—*A.* 2·0 Grams were boiled with 30% sulphuric acid (10 c.c.) for ½ hour, and mixed with sodium hydroxide, when 1·4 g. were removed (unchanged) by ether. On acidifying the alkaline liquor and concentrating, crude 2-thiol-1 : 4-dimethylglyoxaline (0·15 g., m. p. 195°, yield 10%) separated, and gave the pure substance (m. p. 212° alone or mixed) after crystallisation from dilute hydrochloric acid.

B. The hydrochloride (from 7·0 g. of picrate), boiled with 37 c.c. of 5*N*-hydrochloric acid for 6 hours, gave 2-thiol-1 : 4-dimethylglyoxaline (1·32 g., m. p. 212°, yield 59%) and 0·6 g. of very crude ethoxy-base, which gave impure picrate (0·75 g., m. p. 145—148°, not depressed by admixture with the picrate, m. p. 157—158°).

C. Ten grams and 50 c.c. of concentrated hydrochloric acid were heated for 3 hours at 150°. After evaporation, the residue was crystallised from absolute alcohol (mother-liquor L) and gave 2·4 g. (m. p. 226°). After crystallisation from absolute alcohol, it melted at 228° (corr.) and was found by the mixed-melting-point method and analysis to be identical with *2-methylamino-4-methylthiazole hydrochloride* (yield 25%) described below (0·1038, dried at 120°, gave 0·1384 CO_2 and 0·0548 H_2O. C = 36·4; H = 5·9. 0·2034, dried at 120°, gave 0·1770 AgCl. Cl = 21·5. $C_5H_8N_2S,HCl$ requires C = 36·5; H = 5·5; Cl = 21·5%). Identification was confirmed by comparison of the base, hydriodide, and chloroplatinate from each source.

The mother-liquor L was basified with sodium hydroxide, extracted with ether, faintly acidified, and concentrated, when 2-thiol-1 : 4-dimethylglyoxaline (0·15 g.; m. p. 212°, alone or mixed; yield 2%) separated. The ether left an oil, which gave *2-ethylthiol-1 : 4-dimethylglyoxaline picrate* (5·35 g.; m. p. *ca.* 103°; yield 24%). It separates from alcohol in quadrilateral tablets, m. p. 105° (corr.). 0·1016 gave 0·1514 CO_2 and 0·0374 H_2O. C = 40·6; H = 4·1. 0·0818 gave 12·8 c.c. moist N_2 (19·5°, 772 mm.). N = 18·2. $C_7H_{12}N_2S,C_6H_3O_7N_3$ requires C = 40·5; H = 3·9; N = 18·2%. The same salt was obtained from (a) the product of interaction of 2-thiol-1 : 4-dimethylglyoxaline and ethyl iodide at 100°, and (b) the product of boiling 2-thiol-1 : 4-dimethylglyoxaline (1 g.) with 5*N*-hydrochloric acid (20 c.c.) and alcohol (2 c.c.) for 20 hours under reflux (yield 58%).

The *hydrochloride* crystallises from acetone in deliquescent plates, m. p. 125—127° (corr.).

2-Methylamino-4-methylthiazole (XII) was prepared after Traumann (*Annalen*, 1888, **249**, 31) by gently warming a mixture of chloroacetone (12·4 g.) and methylthiocarbamide (12·2 g.), mixing the product with sodium hydroxide, and extracting the base with ether, when a sparingly soluble, basic by-product (2·1 g., m. p. 211° decomp.) separated. The oil left on removing the ether was mixed with absolute alcohol and acidified with gaseous hydrogen chloride, when, on keeping, 6·7 g. of the hydrochloride (m. p. 225°) separated. It crystallised from absolute alcohol in prismatic needles, m. p. 228° (corr.), which were very easily soluble in water. From a strong aqueous solution, sodium hydroxide precipitated the base, which crystallised from alcohol in prisms, m. p. 71·5—72·5° (corr.) (Found : C = 46·8; H = 6·6. Calc., C = 46·8; H = 6·3%). Traumann describes it incorrectly as hygroscopic and gives the m. p. 42°; Young and Crookes (J., 1906, **89**, 59) give m. p. 64°. The hydriodide, fine needles from water, had m. p. 194° (decomp.; corr.) (Traumann, 136°), whilst the chloroplatinate, serrated, prismatic needles, had m. p. 180° (decomp.; corr.) (Traumann, 167°). The base gave with methyl iodide 2-methylamino-3 : 4-dimethylthiazole hydriodide, m. p. 165—166° (corr.) (Young and Crookes, 164°). 2-Methylamino-4-methylthiazole hydrochloride is not completely stable towards hydrochloric acid (5 c.c. to 1 g.) at 150° (3 hours), for only 30% was recovered unchanged in a pure state, but the remainder (of lower m. p.) did not contain 2-thiol-1 : 4-dimethylglyoxaline.

α-Propionacetalylphenylthiocarbamide (XIII) was obtained by mixing α-aminopropionacetal (6·8 g.) with phenylthiocarbimide (6·3 g.) and crystallising the product from alcohol (yield 71%). It formed needles from alcohol, m. p. 110° (corr.). 0·1066 gave 0·2338 CO_2 and 0·0720 H_2O. C = 59·8; H = 7·6. $C_{14}H_{22}O_2N_2S$ requires C = 59·5; H = 7·9%.

Hydrolysis.—7·5 Grams of the above compound were boiled with 20 c.c. of 5*N*-hydrochloric acid for ½ hour under reflux. On concentration, 1·2 g. of 2-thiol-1-phenyl-4-methylglyoxaline separated, and on then working up the mother-liquor as on p. 587 a further 0·2 g. of the thiol compound (total yield 28%) and 7·9 g. of *2-anilino-5-ethoxy-4-methyl-4 : 5-dihydrothiazole picrate* (XV) (yield 64%) were obtained. This salt separates from alcohol, in which it is sparingly soluble in the cold, in yellow needles, m. p. 163—165° (corr.). 0·1010 gave 0·1728 CO_2 and 0·0406 H_2O. C = 46·7; H = 4·5. $C_{12}H_{16}ON_2S,C_6H_3O_7N_3$ requires C = 46·4; H = 4·1%.

2-Thiol-1-phenyl-4-methylglyoxaline (XIV) crystallised from alcohol in well-formed, colourless prisms, m. p. 190—191° (corr.). It is very sparingly soluble in hot water, but soluble in aqueous sodium

hydroxide. 0·1010 gave 0·2328 CO_2 and 0·0508 H_2O. C = 62·9; H = 5·6. $C_{10}H_{10}N_2S$ requires C = 63·1; H = 5·3%.

Acetalylphenylthiocarbamide (2·0 g.) [prepared after Wohl and Marckwald in 80% yield, large prisms from alcohol, m. p. 96° (corr.)], boiled with 5*N*-hydrochloric acid (10 c.c.) for ½ hour, gave, on cooling, pure 2-thiol-1-phenylglyoxaline [1·02 g., m. p. 181—182° (corr.), yield 78%]; after addition of sodium hydroxide, ether collected 0·2 g. of base yielding a picrate (0·25 g.), m. p. 196° alone or mixed with the picrate of the ethoxy-base described below. When the hydrochloric acid was replaced by 30% sulphuric acid (10 c.c.), the yield of the thiol compound was the same, but the recovered ethoxy-base was less pure.

2-*Anilino*-5-*ethoxy*-4 : 5-*dihydrothiazole*. — Acetalylphenylthiocarbamide (12 g.) was stirred into concentrated sulphuric acid (30 c.c.) below 0°. After ½ hour, the solution was poured on to ice, and mixed with sodium hydroxide; ether then extracted the ethoxy-base (10 g., almost pure). It crystallises from moist alcohol in prismatic needles, m. p. 92—93° (corr.). 0·1060 gave 0·2316 CO_2 and 0·0638 H_2O. C = 59·6; H = 6·7. 0·2486 in 16·62 benzene (cryoscopic) gave Δ 0·31°, M = 236. $C_{11}H_{14}ON_2S$ requires C = 59·4; H = 6·3%; M = 222). Wohl and Marckwald give m. p. 94° and composition $C_{11}H_{16}O_2N_2S$. The picrate melted at 198° (corr.); W. and M. give dec. 190°.

Hydrolysis.—A. The ethoxy-base (3 g.) was boiled with 30% sulphuric acid (15 c.c.) for ½ hour, mixed with water (15 c.c.), and cooled. The solution deposited 2-thiol-1-phenylglyoxaline (2·0 g., m. p. 175°, yield 84%), from which the pure substance (1·75 g.) was obtained by crystallisation from water. The mother-liquors, mixed with sodium hydroxide, and extracted with ether, gave 0·25 g. of crude ethoxy-base (semi-crystalline; it gave a picrate, m. p. 185°, which did not depress the m. p. of the ethoxy-base picrate).

B. The ethoxy-base (2 g.) was heated with concentrated hydrochloric acid (10 c.c.) for 3 hours at 150°. On concentrating and adding water, 2-thiol-1-phenylglyoxaline (0·27 g., m. p. 181—182°, yield 17%) separated. After the filtrate had been mixed with sodium hydroxide, ether collected an oil (1·3 g.), which was mixed with picric acid (1·5 g.) in hot alcohol (45 c.c.), when 2-anilinothiazole picrate (0·12 g., m. p. 198—199°, yield 3·3%) separated from the hot solution, followed, on cooling, by *2-ethylthiol-1-phenylglyoxaline picrate* (2·4 g., m. p. 117—118°, yield 61%). It separated from alcohol in yellow needles, m. p. 119—120° (corr.). 0·1044 gave 0·1798 CO_2 and 0·0338 H_2O. C = 47·0; H = 3·6. 0·0776 gave 10·7 c.c. moist N_2 at 16·5° and 772 mm. N = 16·4. $C_{11}H_{12}N_2S,C_6H_3O_7N_3$ requires C = 47·1; H = 3·5; N = 16·2%.

The same salt was obtained readily from the products of interaction of 2-thiol-1-phenylglyoxaline with (*a*) ethyl iodide at 100°, (*b*) hydrochloric acid (5 c.c. of conc. acid to 1 g.) and alcohol (1 c.c.) at 150°.

The base formed an oil, b. p. 310°/772 mm. with slight decomposition. 0·1090 gave 0·2578 CO_2 and 0·0592 H_2O. C = 64·5; H = 6·1. $C_{11}H_{12}N_2S$ requires C = 64·7; H = 5·9%. 2-Thiol-1-phenylglyoxaline melts at 181—182° (corr.) (W. and M., 181°). After heating it (1 g.) with concentrated hydrochloric acid (5 c.c.) for 3 hours at 150°, 0·9 g. was recovered unchanged. The 2-anilinothiazole was identified by comparison of the base and picrate with the substance obtained by Traumann's method (*loc. cit.*) (yield 66%) and its picrate. The bases and a mixture melted at 127—128° (corr.); Traumann gives 126°; Näf (*Annalen*, 1891, **265**, 108) gives 124°. The *picrate* from each source and a mixture had m. p. 198—199° (corr.); this salt is very sparingly soluble in hot alcohol. 2-Anilinothiazole can be recovered quantitatively unchanged after heating with hydrochloric acid (5 c.c. of conc. acid to 1 g.) for 3 hours at 150°.

Acetalyl-m-*xylylthiocarbamide*, prepared from aminoacetal (2·78 g.) and *m*-xylylthiocarbimide (3·3 g.), was added to concentrated sulphuric acid (17 g.) at 0°. After an hour, the liquid was diluted with ice, extracted with ether, which removed 0·2 g. of oil, made alkaline with ammonia, and again extracted with ether, when an oil (4·5 g.) was obtained which did not crystallise on keeping. It was converted into picrate and crystallised fractionally from hot alcohol, when 1·0 g. of the salt described by Marckwald was obtained, having m. p. 142—143° (corr.) (Found: C = 47·4; H = 4·6. Calc., C = 47·6; H = 4·4%). The base regenerated from the pure salt did not crystallise.

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LXXXVII.—*An X-Ray Investigation of Saturated Aliphatic Ketones.*

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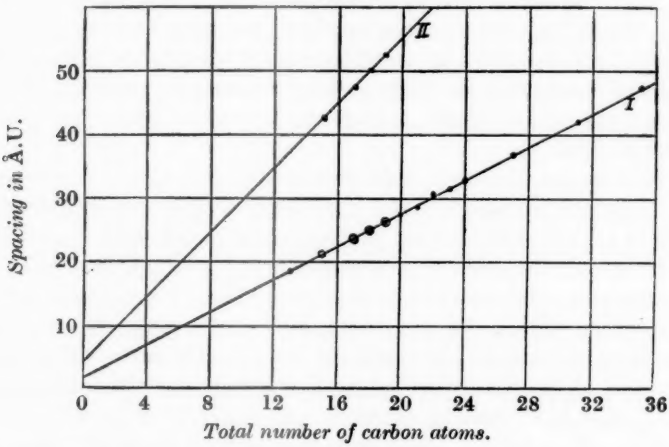
THIS paper is a continuation of the work on *X*-ray measurement of the higher members of the fatty acid series and their esters (Müller, J., 1923, **123**, 2043; Shearer, *ibid.*, p. 3152; Müller and Shearer, *ibid.*, p. 3156) and deals in particular with saturated aliphatic ketones. By an examination of these compounds it was

hoped that confirmation of the suggestions put forward in the previous papers would be obtained and that light would be thrown on the effect on the molecular structure of a variation of the position of the carbonyl group in the ketone molecule.

(1) *Preparation of Ketones.*—The ketones were prepared from the corresponding normal fatty acids by the valuable catalytic method of Senderens (*Compt. rend.*, 1909, **149**, 993); the apparatus used was a modification of that of Pickard and Kenyon (J., 1911, **99**, 56). Five gram-molecules of the more volatile acid were used to one of the higher acid, this proportion yielding convenient amounts of the mixed ketones, which were readily separated from those of higher symmetry by vacuum distillation. The various products were

FIG. 1.



further purified by crystallisation from suitable solvents. It is essential that the initial acids should be free from homologous impurities, as otherwise the ketones cannot be obtained in a pure state.

(2) *Experimental Procedure and Results.*—As in previous experiments, a glass plate carrying a thin layer of the substance was oscillated in an *X*-ray beam (FeKα radiation) and the spectra were received on photographic plates. These spectra consist of a large number of lines the majority of which are successive orders of reflection from one plane in the crystal. This plane has a very much larger spacing than any of the others and its spacing has been shown to bear a close relation to the length of the molecule of the substance under investigation. In a previous paper, arguments were advanced to show that this spacing is probably, within narrow limits, a measure of the length of a single molecule or of two molecules end to end.

It was also suggested that when the molecules contained at one end a chemically active group there was a tendency for the molecules to arrange themselves in pairs, whereas if there was no such active group at the end, no such tendency existed and the *X*-ray spacing measured was a measure of the length not of two, but of a single molecule. The following table gives a summary of the results of the measurements of the principal spacing.

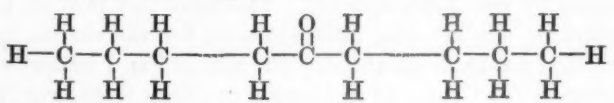
Ketone.	Formula.	M. p.[1]	Spacing.
Di-*n*-hexyl	$C_6H_{13}\cdot CO\cdot C_6H_{13}$	30°	18·7
Methyl *n*-tridecyl	$CH_3\cdot CO\cdot C_{13}H_{27}$	39·5	42·4
Methyl *n*-pentadecyl	$CH_3\cdot CO\cdot C_{15}H_{31}$	48—48·5	47·6
Methyl *n*-hexadecyl	$CH_3\cdot CO\cdot C_{16}H_{33}$	52	50·0
Ethyl *n*-pentadecyl	$C_2H_5\cdot CO\cdot C_{15}H_{31}$	52·5	25·2
Hexyl *n*-undecyl	$C_6H_{13}\cdot CO\cdot C_{11}H_{23}$	45 *	25·2
Methyl *n*-heptadecyl	$CH_3\cdot CO\cdot C_{17}H_{35}$	55·5—56	52·9
Propyl *n*-pentadecyl	$C_3H_7\cdot CO\cdot C_{15}H_{31}$	50	26·3
Ethyl *n*-heptadecyl	$C_2H_5\cdot CO\cdot C_{17}H_{35}$	59·5—60	27·3
Propyl *n*-heptadecyl	$C_3H_7\cdot CO\cdot C_{17}H_{35}$	56 *	28·9
Hexyl *n*-pentadecyl	$C_6H_{13}\cdot CO\cdot C_{15}H_{31}$	54	31·1
Di-*n*-undecyl	$C_{11}H_{23}\cdot CO\cdot C_{11}H_{23}$	69·5	31·6
Hexyl *n*-heptadecyl	$C_6H_{13}\cdot CO\cdot C_{17}H_{35}$	62 *	33·6 (30·8)[2]
Di-*n*-tridecyl	$C_{13}H_{27}\cdot CO\cdot C_{13}H_{27}$	69·5	37·0
Di-*n*-pentadecyl	$C_{15}H_{31}\cdot CO\cdot C_{15}H_{31}$	76—76·5	41·1
Di-*n*-heptadecyl	$C_{17}H_{35}\cdot CO\cdot C_{17}H_{35}$	82·5	47·2

[1] Melting points were determined by the capillary-tube method. The values marked * have not been previously recorded.

[2] In addition to the 33·6 spacing a few orders of a spacing 30·8 also occur in the spectrum. These are probably due to a second crystalline modification (see Müller's paper on the hydrocarbons).

(3) *Interpretation of* X-*Ray Results*.—In Fig. 1 the results are shown graphically, the spacing being plotted against the total number of carbon atoms in the molecule. It will be observed that the ketones group themselves into two sets represented by the straight lines I and II. In either of these sets the continued addition of CH_2 groups to the molecule results in a uniform rate of growth of the spacing, thus confirming the result, previously deduced from the measurements of other series, that the size of this spacing bears a close relation to the length of the molecule. The actual values of the spacings in group I are what we should expect if only a single molecule existed between successive reflecting planes. In group II the spacing suggests a length double that of a single molecule. The condition previously suggested for the existence of a spacing corresponding to the length of a double molecule was that the molecule should possess an active group at its end. The end group of the ketone molecule is CH_3 if the formula be written

(I.)



which, as we shall see later, is the most probable arrangement. Such an end group must be regarded as inactive chemically, and therefore, in accordance with our empirical rule, we should expect to find only one molecule between successive planes. Four of the ketones examined give, however, a spacing corresponding to two molecules. These four are not distributed at random, but are all methyl ketones in which there is only one CH_3 group separating the carbonyl group from the end of the molecule. It would appear, therefore, that in these cases the CO group is sufficiently near the end of the molecule for these methyl ketones to be considered as possessing an active end group—$CO{\cdot}CH_3$. In the ethyl, propyl, etc., ketones, the carbonyl group is too far from the end of the molecule to make its effect felt in the building of the crystal. If this interpretation is correct, it would appear to open up a method for the investigation of the range of action of the oxygen atom.

Further confirmation of this interpretation of the *X*-ray data as closely representing the lengths either of one or of two molecules comes from Fig. 1. If the spacings of the methyl ketones are halved, the points representing them fall, within the limits of experimental error, on the line representing the other members of the series. They are shown in the figure by circles. Typical photographs of groups I and II are shown in the first two spectra of Fig. 3. The first represents methyl heptadecyl ketone, the second propyl pentadecyl ketone. Both contain 19 carbon atoms, but it is clear that the spacing of the methyl ketone is twice that of the other, as is shown by the fact that the 2nd, 4th, 6th, 8th, etc., orders of the methyl ketone coincide with the 1st, 2nd, 3rd, 4th, etc., orders of propyl pentadecyl ketone. This would suggest that, when the spacing corresponds to the length of two molecules, these are so arranged in the crystal that there is little or no overlapping lengthwise of the two molecules. Further, it will be observed that the intercepts on the vertical axis of the lines I and II are approximately 2 and 4 Å.U. This is just what we should expect from the extra hydrogens on the final carbons; in the case of a single molecule these would contribute about 2 Å.U., in the case of a double molecule 4 Å.U., to the spacing.

One of the chief reasons for the examination of the ketone series was the hope of discovering in this way the effect on the molecule of the position of the carbonyl group. The results show that this group has little, if any, effect on the length of the molecule as indicated by the *X*-ray spacing. The mere fact that all the points representing the ketones, after allowing for the double spacing in the methyl group, lie on the straight line in Fig. 1 indicates that the existence of the CO group in varying positions from near the end to

the centre of the molecule has little influence on the length of the molecule. That length appears to be a function of the total number of carbon atoms alone, and the CO group behaves for all practical purposes, as far as the length of the molecule is concerned, in the same way as if it were a CH_2 group. This also enables us to decide whether the graphic formula for a ketone should be written

$$\left.\begin{matrix} C_nH_{2n+1} \\ C_mH_{2m+1} \end{matrix}\right\rangle CO \quad \text{or} \quad C_nH_{2n+1}\cdot CO\cdot C_mH_{2m+1},$$

both of which formulæ are in common use at present. Consider the former formula. If the molecule really conformed to such an arrangement, the length would be determined by the length of a chain of $n + 1$ or $m + 1$ carbon atoms according as n is greater or less than m. In the case of the latter formula the length would be determined by a number, $n + m + 1$, of carbon atoms. Fig. 1 shows immediately that concordant results are obtained when $n + m + 1$ is plotted against the spacing, whereas if $n + 1$ or $m + 1$ were used chaos would result. Again, if the former were the true formula, we should expect such substances as ethyl or propyl heptadecyl ketone to show the same spacing as di-*n*-heptadecyl ketone, whereas the table shows that they are very different. It must, however, be remembered that in the former case the position of the CO group at the end of the molecule would probably result in a crystal combination in which the spacing measured would correspond to twice the length of the molecule. If this were so, then the spacing would be determined by $2n + 2$ or $2m + 2$ according as n or m is the greater. This again is inconsistent with the observed results. We conclude, therefore, that the formula which is consistent with the *X*-ray data is the latter, and these results seem to indicate definitely that, in the solid state, the molecule has approximately this structure.

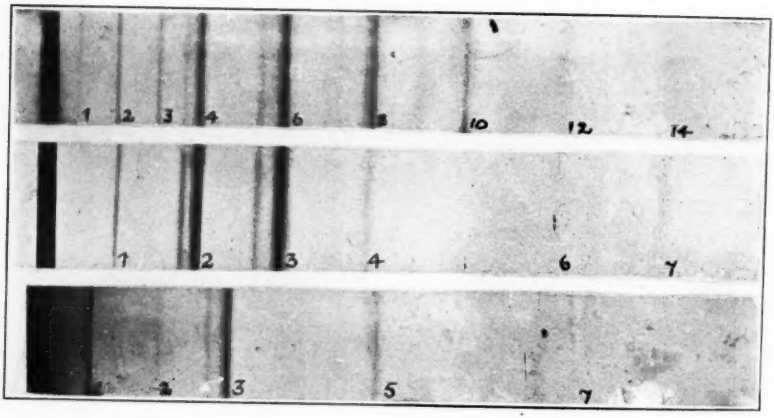
In a previous paper, certain arguments were advanced in support of the assumption that the angle between successive carbon atoms in the chain is the tetrahedral angle of 109° 28′. It was shown that there are three principal types of chain and that the observed rates of increase of length per CH_2 group are consistent with the assumption that the molecules are placed very nearly perpendicular to the principal reflecting planes and the carbon atoms are linked together in one or other of two of these types of chains. From Fig. 1 the average increase of the ketone spacing per CH_2 group is 1·30 Å.U., a value somewhat higher than the larger of the two increments previously found. Although the difference is small, it appears to be outside the experimental error, and it would seem that certain modifications of the suggestions put forward in previous papers may

be necessary. It is proposed shortly to publish a discussion of all the results so far obtained and the bearing of these results on the structure of the carbon chain. If the carbon atom has the same diameter as in diamond, the largest possible increase per carbon atom in a chain subject to the tetrahedral angle condition is 1·26, a value only just smaller than that observed.

Some doubt has been expressed (*e.g.*, Wyckoff, "The Structure of Crystals," p. 379 *et seq.*) as to whether these substances are truly crystalline. It has been suggested that they are in an intermediate state between the solid and the liquid condition. If, for example, the molecules tended to orient themselves perpendicular to the glass surface, it is conceivable that we might get a series of successive layers of equal thickness in which the molecules were all arranged parallel to each other lengthwise. This would give a periodicity parallel to the length of the molecule, but no periodicity in any other direction. The result would be that the *X*-ray spectra would show only reflections from one plane. Whilst the majority of the lines on the plates are successive reflections from such a plane, other lines occur all of which correspond to relatively small spacings; these are not high orders of the main spacing, but are of independent origin, and a "Faser-diagram" photograph made from a small flake shows definitely that they originate in other planes in the crystal. In fact the behaviour of these substances is exactly like that of the ordinary crystal. Owing to their flaky nature, it is particularly easy to obtain reflections from the large-spacing plane, as the process of pressing the substances on to a glass plate tends to produce a special orientation in which these planes are set parallel to the surface of the glass, just as would happen if graphite were treated in the same way. There seems no reason for assuming that these substances differ in any material way from ordinary crystalline matter.

It has been pointed out that there is a difference between the methyl ketones and the others in that the spacing observed for the methyl ketones corresponds to that of planes separated by two molecules and not by a single molecule. It might be expected that this difference would make itself shown in other physical and in chemical ways. The most natural constant to examine is the melting point. The melting point is a function of the energy required to break down the crystalline structure, and it might well be expected that the binding of the methyl ketone molecules in the crystal would be stronger than that of those ketones which show only one molecule between successive planes and in which the CO group is further removed from the end of the molecule. An examination shows that the melting points of the methyl members of a series are

FIG. 3.

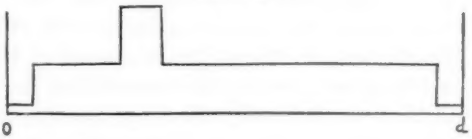


[*To face p. 597.*]

higher than would be expected from an extrapolation from the higher members of the series. It must be remarked, however, that the ethyl ketones also show high melting points, a result which the *X*-ray measurements would hardly anticipate. Perhaps some such property as this is of fairly common occurrence and may form the basis of an explanation of the fact that the first member of a series often differs in properties from the higher members.

A study of the distribution of intensity among the various orders of reflection from the principal plane leads to results which confirm the structure suggested above. It has been pointed out that the position of the carbonyl group does not affect the length of the molecule; it has, however, a very marked influence on the intensity distribution. On certain simple assumptions it is possible to calculate what the intensity distribution should be if the molecule conforms to the proposed structure. The carbon chain may be regarded

FIG. 2.



as a uniform distribution of scattering matter extending over the greater part of the distance between two planes; at the ends where the extra hydrogens occur there will be an almost complete absence of scattering matter, while there will be an excess at that point of the chain where the oxygen atom is situated. Fig. 2 represents diagrammatically such a structure. It is not proposed to enter into a mathematical analysis of the problem, as a full account of the method will be published elsewhere, but the results to be expected may briefly be indicated. If the oxygen occurs at the middle of the chain, as in the di-*n*-ketones, the odd orders will be strong and the even orders weak; if the oxygen is one-third of the way along the molecule, the third, sixth, ninth, etc., orders will tend to disappear; if one-quarter along, the fourth, eighth, etc., orders will be weak, and so on. Half-way between successive minima, positions of maximum intensity will occur. Such predictions are in complete agreement with observation. In Fig. 3, in the third photograph, which represents a di-*n*-ketone, the 1st, 3rd, and 5th orders are well marked, while the even orders are almost non-existent. The second photograph represents propyl pentadecyl ketone, where the oxygen atom is about one-fifth of the way along; the higher orders do not show well in the reproduction, but there is a minimum at the fifth order with a corresponding maximum

between the second and third orders. The case of the di-*n*-ketones is of peculiar interest, as the intensity distribution shown by these compounds is found in many other series, *e.g.*, the fatty acids. In all the other cases where such a distribution has so far been observed, the *X*-ray spacing corresponds not to the length of a single molecule, but to that of two molecules. In a previous paper it was suggested that when two molecules existed lengthwise between two successive planes they were oriented in opposite directions. In the case of these ketones, we have to deal only with a single molecule, but it is clear that a molecule whose formula is $C_nH_{2n+1}\cdot CO\cdot C_nH_{2n+1}$ may be regarded as equivalent from this point of view to two half-molecules, $C_nH_{2n+1}\cdot(\frac{1}{2}CO)$, placed end to end in opposite directions. The fact that we find the same intensity distribution in the di-*n*-ketones and in the fatty acid series appears to be new evidence in favour of the suggestion that the two acid molecules which occur end to end between successive planes have their carboxyl groups oriented in opposite directions. Provided that the oxygen atom is kept at the same fractional distance from the end of the molecule, the intensity distribution is almost independent of the number of carbon atoms in the chain, just as, in cases where the chain is continuous, we find that the intensity distribution remains practically unaltered, although the number of carbons is varied within wide limits.

We see, therefore, that from a study of the *X*-ray spacing it is possible to determine the number of carbon atoms in the ketones, whilst a consideration of the intensity distribution enables us to locate, within reasonably narrow limits, the position of the carbonyl group.

In conclusion, we have much pleasure in expressing our great indebtedness to Professor Sir W. H. Bragg, F.R.S., for his never-failing interest in the work and his many helpful suggestions made during its progress. The research was in part financed by the Department of Industrial and Scientific Research, whose help is gratefully acknowledged. For the methyl hexadecyl ketone we are indebted to Prof. G. T. Morgan, F.R.S., and Mr. E. Holmes of Birmingham University. The other chemicals used were prepared in this laboratory with the able assistance of Mr. A. S. C. Lawrence.

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[*Received, January 26th*, 1925.]

LXXXVIII.—*Further X-Ray Measurements on Long-chain Compounds* (n-*Hydrocarbons*).

By Alex Müller and William Bristow Saville.

Extending the work on *X*-ray investigations of long-chain compounds (Müller, J., 1923, **123**, 2043; Shearer, *ibid.*, p. 3152; Müller and Shearer, *ibid.*, p. 3156), this paper deals with new measurements made on normal hydrocarbons. The substances which had been investigated previously all contained at least one oxygen atom per molecule. It has now been shown that the absence of the oxygen atom has no appreciable influence on the reflecting power for *X*-rays, and this leads to the conclusion that the chain itself plays a predominant part in the reflection phenomena.

The technique was exactly the same as in the previous work. The substance was spread in a thin layer on a small strip of glass. The strip was then mounted on the table of an *X*-ray spectrometer and the spectra were photographed by exposing the substance to homogeneous *X*-rays.

Preparation of the Normal Saturated Hydrocarbons.—The hydrocarbons were prepared by reduction of the corresponding ketones by a modification of Clemmensen's process (*Ber.*, 1913, **46**, 1837).

The pure ketone (2·5—5 g.; prepared by Senderens's method) is heated under reflux on the water-bath with 50 g. of amalgamated zinc and five successive 50 c.c. portions of equal volumes of concentrated hydrochloric acid and alcohol saturated at room temperature with hydrogen chloride. For rapid reduction it is essential to have a vigorous evolution of hydrogen. When the reaction slackens, the mixture is cooled, the liquor decanted, and a further 50 c.c. of the acid mixture added to the solid. Five such treatments are usually sufficient. The total time required is about 3 hours. The hydrocarbon is purified by treatment with warm concentrated sulphuric acid and crystallised from alcohol or benzene. The yield is almost theoretical.

Discussion of the Results.—It has been pointed out in the introduction that the reflecting power for *X*-rays of the hydrocarbons is of the same order of magnitude as that of the fatty acids, esters, and alcohols. The conclusion was drawn that the chain in these compounds has a predominant influence on their reflecting power. The spectra obtained from the hydrocarbons are very similar to those obtained from the substances previously investigated. One set of lines belongs to a comparatively large spacing. This spacing, d_1, increases proportionally to the number of carbon atoms in the substance. Another set of lines can be related to spacings which

TABLE I.

n-Hydrocarbon.	Formula.	M. p.	Main spacing. d_1.	Side spacings. d_2.	d_3.	d_4.	d_5.	d_6.	Ketone used.
Heptadecane	$C_{17}H_{36}$	23°	24·3	4·25	3·93	—	2·54	2·32	Methyl *n*-pentadecyl.
Octadecane	$C_{18}H_{38}$	28	25·9	—	4·0	—	—	—	Ethyl *n*-pentadecyl.
Nonadecane	$C_{19}H_{40}$	32	26·9	4·22	3·84	—	2·52	2·25	Methyl *n*-heptadecyl.
Eicosane	$C_{20}H_{42}$	37	28·0	—	3·9	—	—	—	Ethyl *n*-heptadecyl.
Heneicosane	$C_{21}H_{44}$	41	29·4$_5$	4·17	3·77	3·01	2·50	2·25	Propyl *n*-heptadecyl.
Tricosane	$C_{23}H_{48}$	47	32·2	—	—	—	—	—	Di-*n*-undecyl.
Tetracosane	$C_{24}H_{50}$	51	33·0$_5$	4·18	3·80	3·02	2·50	2·25	Hexyl *n*-heptadecyl.
Heptacosane	$C_{27}H_{56}$	59·5	37·1	4·17	3·77	3·01	2·51	2·25	Di-*n*-tridecyl.
Hentriacontane	$C_{31}H_{64}$	69	43·0	4·14	3·74	2·99	2·49	2·21	Di-*n*-pentadecyl.
Pentatriacontane	$C_{35}H_{72}$	74	47·7	—	—	—	—	—	Di-*n*-heptadecyl.

			d'_1.	Side spacings.					
Octadecane, second form		—	23·9	4·58	3·80	3·66	2·61	—	2·05
Eicosane „ „		—	26·2	4·63	3·82	3·61	2·59	2·12	2·03

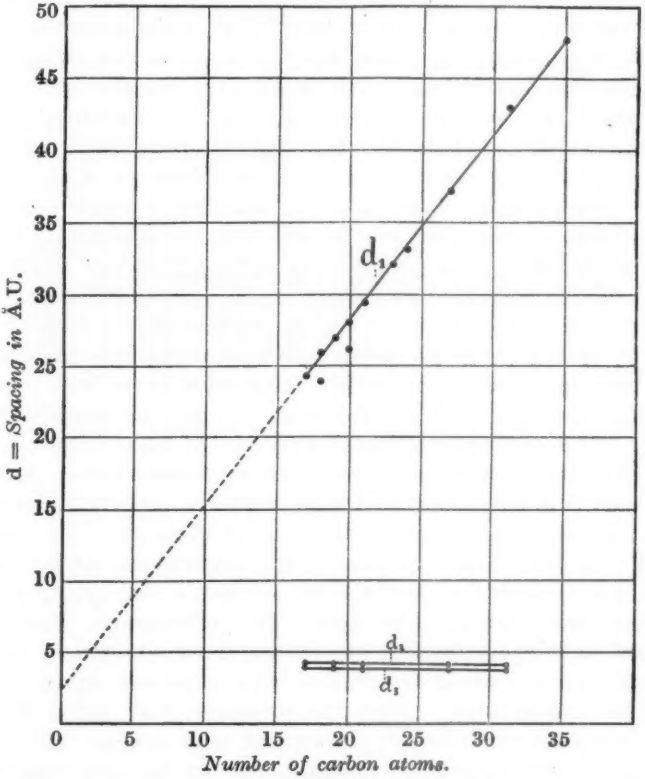
The spacings are given in Ångström units. 1 Å.U. = 10^{-8} cm.

The side spacings of tricosane and pentatriacontane have not been measured.

The side spacings of the first form of octadecane and eicosane were not well defined. The measurements are only approximate.

are almost independent of the number, N, of carbon atoms. These independent or side spacings have been investigated separately by a transmission method. The two strongest lines in the side spacing group show a slight shift away from the central line on the photograph as the number of carbon atoms increases. The side spacings d_2 and d_3 show, therefore, a slight decrease with increasing number of carbon atoms. This means that the transverse dimensions of the

FIG. 1.



unit cell are also to a small extent a function of N.* The numerical data are given in Table I. A large number of lines were found which belong to the side spacing group; only the five strongest, d_2, d_3, d_4, d_5, and d_6, are given in the table. Fig. 1 shows the linear increase of d_1 with the number of carbon atoms.

The long spacings have been measured for ten different hydrocarbons, the number of carbon atoms ranging from 17 to 35. The

* Three of the fainter lines in the side spacing group (d_4; d_5; d_6) show only a very small variation.

increase of d_1 per carbon atom was constant within the limits of experimental error. This has been observed for all the substances investigated so far. The numerical value of this increase is, in the case of hydrocarbons, very nearly 1·3 Å.U. per carbon atom, which is larger than any corresponding value for other substances and is considerably larger than one would have expected from the theory advanced by Müller and Shearer (*loc. cit.*, p. 3158).

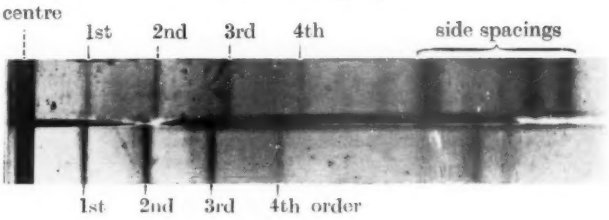
The picture of these long chains as given in the previous paper has therefore to be modified. The experimental data available so far are insufficient for a complete discussion of the structure of any of these long-chain compounds, but the latest measurements seem to indicate that an additional variable has to be introduced to explain their behaviour. One can obviously give up the parallelism between the long axis of the chain and d_1. Another possibility consists in the introduction of several values for the diameter of the carbon atom. These points will be discussed later in a separate paper.

A further experimental result will now be described. It was observed that the spacings of the C_{18} and C_{20} hydrocarbons did not agree with the constant increase of length per carbon atom. This happened when the substances were kept at room temperature. When, however, the temperature was changed by a certain amount, another set of lines appeared on the plates. This other set of lines belonged to a long spacing which differed from the first by something like 6—7%. The existence of these two sets of lines indicates that these substances have more than one crystalline form. Each of these modifications is stable if kept within a certain temperature range. It was further noticed that one of these two long spacings agreed with the normal increase. One experiment carried out on octadecane consisted in melting the substance and giving a short exposure immediately afterwards. The photograph, which was obtained while the substance was cooling down, showed two sets of long spacings, the longer and normal being relatively strong and the other one rather weak. After the substance had cooled down to room temperature, another photograph was taken. The longer spacing had now completely disappeared. In the next experiment (with eicosane), the temperature was controlled by means of a small heater mounted on the spectrometer table. The eicosane was melted and allowed to solidify. When it assumed the transparent solid state, an *X*-ray photograph was taken. As the temperature fell a sudden change occurred, the solid becoming white and opaque.*

* Garner and Randall (J., 1924, **125**, 369), who have studied the phenomena which occur during the solidification of several members of the fatty acid series, conclude that an internal rearrangement takes place after the substance has gone through the transparent stage.

PLATE 1.

Eicosane, $C_{20}H_{42}$.



$d'_1 = 26{\cdot}2$ Å.U. $d_1 = 28{\cdot}1$ Å.U.

[*To face p.* 602.]

A second photograph was then taken. The results agreed with expectation. The transparent and the opaque form differed in their crystalline structure. Both the long and the side spacings were different for the two modifications. The numerical values for the two sets of long spacings were: Octadecane, $d'_1 = 23{\cdot}9$ Å.U.; $d_1 = 25{\cdot}9$ Å.U.: eicosane, $d'_1 = 26{\cdot}2$ Å.U.; $d_1 = 28{\cdot}0$ Å.U. d_1 refers to the transparent modification, d'_1 to the opaque one. Plate I shows an enlargement of the spectrograms obtained from the two modifications of eicosane. The behaviour of octadecane and eicosane is not unique. All observations on the solidification process seem to indicate that such behaviour is a general property of this type of chemical compound.

In the paper on fatty acids it was mentioned that the first, third, fifth . . . order of the long spacing give very much higher intensities of reflection than the second, fourth, sixth . . . order. The hydrocarbons behave differently. There is no alternation between the odd and the even orders. The intensity of the lines decreases gradually as the order gets higher. Dr. Shearer has shown by calculation that these facts are closely connected with the linking of the molecules in the unit cell.

Summary.

Certain normal hydrocarbons have been investigated by means of *X*-rays. Two typical sets of spacings are common to all the substances, one relatively large spacing, which increases linearly with the number of carbon atoms in the substance, and another set, which is very nearly independent of this number. The two strongest lines in the side spacing group coincide very closely with corresponding lines given by fatty acids, esters, and alcohols.

The increase per carbon atom of the long spacing is too large to be accounted for by the longest of the tetrahedral chains.

Two crystalline modifications have been detected for octadecane and eicosane.

In conclusion, the authors wish to express their best thanks to Sir William Bragg for his kind interest in this work. The *X*-ray part of this investigation has been made possible by the support of the Department of Scientific and Industrial Research.

DAVY FARADAY LABORATORY,
ROYAL INSTITUTION. [*Received, January 26th*, 1925.]

LXXXIX.—*The Rotatory Dispersive Power of Organic Compounds. Part XV. Borneol, Camphor, and Camphorquinone. The Origin of Complex and Anomalous Rotatory Dispersion.*

By THOMAS MARTIN LOWRY and JOHN OUTRAM CUTTER.

1. *Introductory.*

THE three preceding papers of this series have dealt with "*simple rotatory dispersion*," *i.e.*, with rotations which can be expressed by one term of Drude's equation, up to the limit of accuracy of the observations, and over a range of wave-lengths extending to the point at which the medium ceases to be completely transparent. Four earlier papers were devoted to the "*anomalous rotatory dispersion*" of methyl and ethyl tartrate; but the data for these esters can be expressed with similar accuracy by the same general equation when two terms of opposite sign are used instead of one. These observations had two important features in common, namely, (i) that in neither group of compounds could a band of selective absorption be detected by the methods at present available, which show only a general absorption spreading in from the inaccessible ultra-violet region; (ii) that the asymmetric system was always very simple, *e.g.*, one asymmetric carbon atom in octyl alcohol, two of identical type in the tartaric esters, and none at all in Pope's acid. The present and following papers describe an attack on more complicated systems, since the substances used (i) contain 2, 3, or 4 dissimilar asymmetric carbon atoms and (ii) exhibit a selective as well as a general absorption of light.

The investigation of these more difficult cases was undertaken without any preconceived ideas as to the complex character of the dispersion which they exhibit, or the possible relation of the rotatory dispersion to the absorption of the compounds, which was only taken up after the whole of the rotations had been measured and expressed by means of equations. These equations are, therefore, purely experimental in character, and were not biassed by theoretical considerations of any kind, except as a result of a well-founded conviction in the validity of Drude's equation in its most general form. The work was indeed begun with a mistaken expectation (based on a rough graphical analysis of a few earlier data) that the rotatory dispersion of camphor would prove to be *simple*, but might be rendered complex by the development of a new asymmetric carbon atom in the stereoisomeric

α- and α′-derivatives. The new experiments soon proved, however, the futility of this expectation, and revealed the fact that we had plunged much more deeply than we desired into the problem of complex rotatory dispersion; it is, indeed, only since the development by Lowry and Walker of the theory of "induced asymmetry" in unsaturated compounds that we have been able to form a clear picture of what was happening, or to give a plausible explanation of these very puzzling phenomena. Since these three papers will be followed by others dealing with the rotatory dispersion of unsaturated compounds, in which the same principles will be applied, it will be convenient to explain in advance the views which we hold in reference to the origin of complex and anomalous dispersion in compounds of this type.

2. *A General Theory of the Origin of Anomalous Rotatory Dispersion.*

It has recently been stated (Astbury, *Chem. and Ind.*, 1924, 43, 332) that "no sound general theory of anomalous rotatory dispersion exists." This statement we regard as incorrect, as it has been known since 1836 that *anomalous rotatory dispersion in transparent media is produced by the superposition of two normal rotations of opposite sign and unequal dispersion.* R. W. Wood has indeed directed attention to the fact that "spurious" anomalies may occur in the region between two absorption bands, and has even suggested that the anomalous rotatory dispersion of tartaric acid may be a case of this kind, depending on the combined influence of an ultra-violet and an infra-red absorption; but this view receives no support from measurements of the rotatory dispersion of this series of compounds, since these can be expressed completely as the sum of two simple partial rotations *of which the characteristic frequencies are both in the ultra-violet region.* This type of anomaly has, in fact, never been observed in any optically-active compound. Although, therefore, we may admit the theoretical possibility of a "spurious" anomalous rotatory dispersion, even in transparent media, the explanation given by Biot in 1836 still covers the whole of the experimental data.* The only point

* The anomaly discovered by Cotton in 1895 (*Compt. rend.*, 1895, **120**, 989, 1044; *Ann. Chim. Phys.*, 1896, [vii], **8**, 347) in the optical rotations *when passing through an absorption band* is so familiar in other optical properties and appears to be so inevitable, that, as R. W. Wood says, "there is nothing anomalous about it." It is therefore only because anomalous rotatory dispersion is observed *in transparent media*, and *at wave-lengths differing widely from those of selective absorption*, that a special explanation is called for, and this is provided by the fact that optical rotations are of two signs, whereas refractions are all of similar sign.

of controversy is therefore the origin of the two opposite partial rotations in any particular case, and not the general theory that anomalies are produced by their superposition.

It is, however, necessary to emphasise the fact that *no theoretical significance whatever can be attached to the distinction between normal and anomalous rotatory dispersion*, when both are of a type which can be represented by a Drude equation containing two terms of opposite sign,* since a minute change in the rotation-constants of the equation, *e.g.*, as a result of an unimportant change of temperature or of concentration, may suffice to alter the type of dispersion from normal to anomalous,† or *vice versa*. It is therefore of primary importance to determine (i) whether the dispersion can be expressed by one term of Drude's equation, or requires two or more terms of this equation to represent it, *i.e.*, whether the dispersion is simple or complex, and (ii) in the case of a two-term equation, whether the partial rotations are *of similar sign* or *of opposite signs*, since these are much more fundamental facts than a mere reversal of sign in the algebraic sum of two opposite partial rotations, which is all that is implied in the change from normal to anomalous dispersion. Moreover, even on the experimental side, the classification of dispersions as "normal" and "anomalous" is no easier than the classification as "simple" and "complex," ‡ which has been put forward to supplement and not to replace the older system.

3. *Methods of Superposing Opposite Partial Rotations.*

As long ago as 1914, in discussing the origin of the anomalous rotatory dispersion of ethyl tartrate, it was suggested by one of us (*Trans. Faraday Soc.*, **10**, 100), in complete agreement with the views of Tschugaev, that anomalies such as these could be produced by superposing the opposite rotations of (i) *two molecules*, (ii) *two radicals* in one molecule, or (iii) *two electrons*, *e.g.*, in one molecule or in one crystal. It is now possible to divide these three classes further into six principal types as follows:

(a) *Optical superposition of two separate media*, as observed by

* See footnote, p. 608.

† This distinction hinges on the question whether the dispersion curve just crosses or just fails to cross the axis of zero rotation.

‡ Thus $[\alpha] = 18{\cdot}0/(\lambda^2 - 0{\cdot}03) - 19{\cdot}0/(\lambda^2 - 0{\cdot}06)$ would give a *normal* dispersion, whilst $[\alpha] = 19{\cdot}0/(\lambda^2 - 0{\cdot}03) - 18{\cdot}0/(\lambda^2 - 0{\cdot}06)$ would give an *anomalous* dispersion. Since the anomalies would all be in the infra-red, it would be just as difficult to distinguish experimentally between the normal and the anomalous dispersion as it is to distinguish between a simple and a complex dispersion when the latter is produced by two partial rotations of the same sign and with dispersion constants of similar magnitude.

Biot in 1836 (*Compt. rend.*, **2**, 543), on balancing a column of lævorotatory turpentine against a column of dextrorotatory oil of lemon.

(b) ***Mixing of two fluid media***, as realised by Biot (*loc. cit.*) on mixing oil of turpentine and oil of lemon in a single tube; by von Wyss (*Wied. Ann. Phys. Chem.*, 1888, [ii], **33**, 567) by mixing turpentine and camphor in the same solution; and by Tschugaev (*Z. physikal. Chem.*, 1911, **76**, 469) by mixing lævorotatory menthone with dextrorotatory *iso*menthone. In all these cases, the two oppositely-active molecules were stable in the solution, and not interconvertible under the conditions then prevailing.

(c) ***Formation of two molecular types from one optically-active compound***, as suggested by Arndtsen in 1858 (*Ann. Chim. Phys.*, 54, 421). One of these types will usually be the same as in the solid crystalline phase (L. Longchambon, *Thesis*, Paris, 1923; *Compt. rend.*, 1924, **178**, 951; Lowry and Austin, *Nature*, 1924, **114**, 430), but the other may be produced either (i) *by association with the solvent*, including the formation of *molecular compounds*, of *hydrated* or *solvated ions*, and of products of *reversible hydrolysis* or *esterification*; (ii) *by polymerisation*, *dissociation*, or *isomeric change of the solute*. In the absence of a solvent, however, only cases of group (ii) are possible.

(d) ***Presence of oppositely-active radicals in one molecule***, as in the *l*-menthyl *d*-camphorsulphonate of Tschugaev (*Trans. Faraday Soc.*, 1910, **10**, 73). It is open to discussion whether the formation of salts from oppositely-active acids and bases should come under this heading, or whether the active ions should be treated as independent molecules, and their solutions regarded as mixtures of type (b) above.

(e) ***Induced asymmetry in unsaturated molecules.*** It has recently been suggested (Lowry and Walker, *Nature*, 1924, **113**, 565) that an unsaturated group in an asymmetric molecule, *e.g.*, the >C=O group in camphor, may acquire an induced asymmetry and thus itself become optically active. This hypothesis has the effect of transferring a large number of cases of anomalous dispersion from Drude's class (f) below to a variant of Tschugaev's class (d) above, since the two opposite partial rotations, instead of being attributed merely to the existence of two natural frequencies in a single molecule, are assigned to different radicals or groups of electrons in the molecule. These cases then differ from Tschugaev's type (d) only in that the presence of a low-frequency term in the dispersion equation is ascribed to the *induced* asymmetry of an unsaturated group (in a molecule already containing a centre of fixed asymmetry) instead of a second centre of *fixed* asymmetry in the molecule.

(f) *Existence of two natural frequencies* (i) *in a single crystal*, (ii) *in a single molecule.* (i) *Crystals with two natural frequencies.* Drude regarded anomalous rotatory dispersion as due to the superposition of the partial rotations of two electrons moving in an asymmetric field, with unequal periods of vibration, and in spirals of opposite sign. No case of anomalous rotatory dispersion has yet been recorded in a transparent crystalline medium; but since the two ultra-violet terms in the dispersion-equation of quartz are of opposite sign, it is merely an accident that the relative magnitude of the two partial rotations is such as not to give rise to anomalous dispersion; * all the common anomalies would indeed appear immediately if the high-frequency term were multiplied by 4. In the case of quartz, Drude's opposite types of asymmetrically-moving electrons must obviously exist *in a single crystal lattice* and *in a single type of molecule*, so that none of the first three methods (a), (b), and (c) of explaining its "quasi-anomalous" dispersion can be applied. Since, however, we may hope ultimately to be able to assign the two ultra-violet terms to two different asymmetric complexes in the crystal-lattice (*e.g.*, one depending mainly on a dissymmetric arrangement of the silicon atoms and of the electrons associated with them, and the other on a dissymmetry of the oxygen groups in the crystal aggregate), we can scarcely expect to maintain class (f) (i) as a totally distinct type of anomalous dispersion. The complex dispersion of quartz appears indeed to differ from type (d) only in that the asymmetric radicals of Tschugaev's molecules are stable and survive dissolution, whilst those of quartz are only found in the polymerised aggregates of the crystal, and disappear when these aggregates are broken up.

(ii) *Molecules with two natural frequencies.* It was obviously possible, on Drude's theory, for two dissimilar types of asymmetrically-moving electrons to appear in the same molecule as well as in the same crystal, giving rise to two absorption bands

* Such cases would be described accurately as "potentially anomalous." Hunter, however, applies this term to the "normal" portions of a totally anomalous curve, *i.e.*, to that half of the curve, lying on one side of the maximum, in which α increases as λ diminishes, so that $d\alpha/d\lambda$ is negative. It should be noticed that this definition is unsatisfactory, in that it includes a section of the curve, between the maximum and the point of inflexion, in which $d\alpha/d\lambda$ decreases in magnitude instead of increasing as λ diminishes, so that its anomalous character is obvious rather than merely potential. In order to avoid ambiguity, it is suggested that the term *quasi-anomalous* should be applied to cases such as quartz, in which a *complex dispersion is produced by partial rotations of opposite sign*, but of such a character that α, $d\alpha/d\lambda$, and $d^2\alpha/d\lambda^2$ are of the same sign throughout the region of transparency lying on the "long wave-length" side of the nearest absorption band.

and to two partial rotations of corresponding frequencies. In the case of organic compounds, however, there are good experimental reasons for ascribing each absorption band to some particular radical in the molecule. The corresponding partial rotations may therefore also be ascribed to these radicals, a view that has already been urged under (e) in the case of unsaturated radicals. In all such cases, the dispersion would then again be of the same general type as (d) or Tschugaev's class. A possible exception, in which the transfer to class (d) could not be effected, would arise if it could be proved that a single asymmetric centre possessed two natural frequencies and gave rise to two bands; but the real existence of such a case, and the consequent necessity of recognising a separate class (f) (ii), is at present a matter of pure speculation. The idea that these two frequencies could give partial rotations of opposite sign, and so produce a totally anomalous dispersion, is even less plausible, and therefore need not be considered at present.

Since any of these six methods of superposing opposite partial rotations may give rise to a complex or an anomalous dispersion, there is no justification for singling out any one of them as a unique cause of anomalous rotatory dispersion. Thus the recent work of Longchambon provides further confirmation of the view that the anomalous dispersion of tartaric acid and its esters should be assigned to class (c). On the other hand, the quasi-anomalous dispersion of borneol, with three fixed centres of asymmetry, is assigned to class (d); and that of camphor to class (e), although some further complexity may be introduced by the formation of unstable "molecular compounds" of camphor with the solvent. Again, the complex dispersion, which so often appears on passing from an optically-active alcohol to its esters, may be due to the development of a partial rotation of opposite sign in the carbonyl radical of the unsymmetrical molecule, just as in the case of camphor. Finally, the complex dispersion of quartz must be assigned provisionally to class (f) (i), until it is possible to distinguish the asymmetric centres which give rise to the various partial rotations.

4. *Discussion of Experimental Results.*

(a) *Scope of the Measurements.*—The present paper includes measurements of the rotatory dispersion of camphor in benzene, *cyclo*hexane, and acetone, and of borneol and camphorquinone in benzene. The camphor was sublimed, and crystallised from *cyclo*hexane, without change of rotatory power; the borneol was crystallised three times from benzene, and the camphorquinone to constant melting point at 198°.

The solvents were selected mainly with a view to adequate

purification, *e.g.*, in the case of benzene and *cyclo*hexane, by freezing until the melting points were constant at 5·54° and 6·28° and the boiling points were 80·2° and 80·9° (corr.); in the case of acetone, by forming a compound with sodium iodide (J., 1913, **103**, 1255). Benzene was used most frequently, since it is easily dried, and gives solutions of a high degree of concentration; it was only at a later stage, when it was desired to compare the rotatory dispersion with the selective absorption of the solute, that this choice was found to be disadvantageous. It is, however, remarkable that *a solution of camphor in benzene is less opaque to ultra-violet rays than a solution in* cyclo*hexane* (compare Gifford and Lowry, *Proc. Roy. Soc.*, 1923, **104**, 434), which transmits very little ultra-violet light. This greater transparency, which made it necessary to replace the glass prisms of the spectrograph by quartz, in order to reach the working limit of transmission of the solution in benzene, is perhaps due to a mutual saturation of the "residual affinities" of the camphor and benzene.

The results recorded vary considerably in value, according to the concentration of the solution, the number and range of wave-lengths used, and the labour incurred in repeating the readings in order to diminish the errors of observation. Thus, Table I, for a concentrated solution in benzene, which includes 41 wave-lengths from 6708 to 3599 Å.U., may be regarded as a "standard" series, in which every effort was made to secure the highest degree of accuracy that can be reached with our present equipment and method, since the visual observations are based on two series of readings with solutions prepared independently by weight, and four such solutions were used for the photographic readings. On the other hand, Table V, for camphorquinone in benzene, includes only 9 wave-lengths in the red to green portion of the spectrum, which is all that can be used for visual readings of a strong solution. The other tables are intermediate in value between these two extremes.

(b) *Form of the Curves.*—All the equations were in the first instance empirical, the only object being to find an algebraical expression which would fit the experimental data. Any theoretical deductions are therefore an after-thought. It is, however, noteworthy that the "simple" equation for camphorquinone has a dispersion-constant, $\lambda^2 = 0{\cdot}2235$, $\lambda = 4730$ Å.U., which corresponds closely with the maximum of selective absorption, although this wave-length is 30 to 80 Å.U. longer than that of the uncorrected position of the "head of the absorption-band." This equation appears, therefore, to have a real theoretical significance, although the simplicity of the observed rotatory dispersion may

perhaps be due to the cancelling out of two high-frequency partial rotations (compare J., 1924, **125**, 2520). In the same way, the two-term equation, which expresses in so satisfactory a manner the rotatory power of camphor in benzene, appears to have a real physical meaning, since the low-frequency term has a dispersion-constant, $\lambda^2 = 0{\cdot}08720$, $\lambda = 2950$ Å.U., which again corresponds with a wave-length about 70 Å.U. greater than that of the observed "head" (at 2880 Å.U.) of the absorption band of a thin film of camphor in benzene (J., 1924, **125**, 1923). In view, however, of the difficulty of analysing the high-frequency component of a dispersion which is already dominated by a partial rotation of low-frequency, we prefer to leave open the question whether this component is really simple, *e.g.*, whether the characteristic frequencies of the two fixed centres of asymmetry, to which this term must be attributed, are identical or merely similar in magnitude.

The remaining equations contain only three constants, since one of the dispersion-constants has been omitted in precisely the same way as in Drude's equation for quartz.* Equations such as these can have no precise theoretical significance, since it has already been established that the two dispersion constants of a four-constant equation can often be varied appreciably without producing any important alteration in the form of the curve,† provided that they are altered simultaneously, *e.g.*, in such a way that their *sum* is kept constant ‡ (Lowry and Dickson, J., 1915, **107**, 1186). It must therefore be assumed that *the low-frequency dispersion-constant of a two-term equation is vitiated whenever the high-frequency dispersion-constant is neglected.* This possibility

* It is noteworthy that a three-constant equation often gives results which cannot be improved by using a fourth constant. This would be expected in all cases in which the high-frequency term is small in magnitude; but in other cases it may be suspected that a term of the type k/λ^2 indicates the presence of two partial rotations of opposite sign, exactly as in the case of a pseudo-simple dispersion which nearly obeys Biot's law (J., 1924, **125**, 2519).

† The absolute values of these constants are therefore obviously much less exact than the values given for the purpose of calculation.

‡ The two-term equation can be rewritten thus:

$$[\alpha] = \frac{k_1}{\lambda^2 - \lambda_1^2} + \frac{k_2}{\lambda^2 - \lambda_2^2} = \frac{\lambda^2(k_1 + k_2) - (k_2\lambda_1^2 + k_1\lambda_2^2)}{\lambda^4 - \lambda^2(\lambda_1^2 + \lambda_2^2) + \lambda_1^2\lambda_2^2}.$$

Since we are considering the region in which λ^2 is greater than λ_1^2 or λ_2^2, the terms in the numerator and denominator are arranged in order of decreasing magnitude. As a first approximation, the rotation will be altered least if we keep $(k_1 + k_2)$ constant in the numerator and $(\lambda_1^2 + \lambda_2^2)$ constant in the denominator. This relation is valid whether k_1 and k_2 are of the same sign or of opposite signs.

Table I.

Rotations of d-*Camphor in Benzene* (*conc. solution*).

33·827 Gms. of camphor in 100 gms. of solution.
Density 0·90793. Length of tube 6 dcm.

$$[\alpha] = 0{\cdot}5427\ a. \qquad [M] = 1{\cdot}5213\ [\alpha].$$

$$[\alpha] = \frac{29{\cdot}384}{\lambda^2 - 0{\cdot}08720} - \frac{20{\cdot}138}{\lambda^2 - 0{\cdot}05428}$$

(a) *Visual Readings.*

Wave-length.	Specific rotations. Obs.	Cal.	Diff.	Wave-length.	Specific rotations. Obs.	Cal.	Diff.
Li 6707·8	29·78°	30·12°	−0·34°	*Fe 4595*	*108·5°*	*108·8°*	*−0·3°*
Cd 6438·5	33·85	33·88	−0·03	*4500*	*119·4*	*119·0*	*+0·4*
Zn 6362·3	35·10	35·09	+0·01	*4408*	*130·2*	*130·6*	*−0·4*
Na 5893·0	44·01	44·27	−0·26	*4332*	*141·1*	*141·3*	*−0·2*
Hg 5790·7	46·75	46·80	−0·05	*4266*	*152·0*	*152·3*	*−0·3*
Cu 5782·2	46·85	47·02	−0·17	*4208*	*162·8*	*163·1*	*−0·3*
Hg 5769·6	47·29	47·34	−0·05	*4157*	*173·6*	*173·4*	*+0·2*
Cu 5700·2	48·95	49·22	−0·27	*4104*	*184·5*	*185·3*	*−0·8*
Hg 5460·7	56·72	56·72	±	*4055*	*195·4*	*197·6*	*−2·2*
Cu 5218·2	66·45	66·41	+0·04	*4022*	*206·2*	*206·8*	*−0·6*
Cu 5153·3	69·52	69·47	+0·05	*3986*	*217·1*	*217·5*	*−0·4*
Cu 5105·5	71·95	71·85	+0·10	*3953*	*227·9*	*228·0*	*−0·1*
Cu 5085·8	73·01	72·88	+0·13	*3919*	*238·8*	*239·9*	*−1·1*
Zn 4810·5	90·21	90·11	+0·10	*3892*	*249·6*	*250·0*	*−0·4*
Cd 4799·9	92·23	90·90	+1·33	*3864*	*260·5*	*261·4*	*−0·9*
Zn 4722·2	97·37	97·07	+0·30	*3838*	*271·3*	*272·4*	*−1·1*
				3815	*282·2*	*283·0*	*−0·8*
				3793	*293·0*	*293·8*	*−0·8*
(b) *Photographic Readings.*				*3754*	*314·7*	*314·6*	*+0·1*
Fe 5233	*65·1*	*65·7*	*−0·6*	*3640*	*390·7*	*391·6*	*−0·9*
5042	*76·0*	*75·3*	*+0·7*	*3599*	*428·7*	*426·7*	*+2·0*
4860	*87·0*	*86·8*	*+0·2*				
4707	*97·7*	*98·3*	*−0·6*				

appears to have been overlooked by Pickard and Hunter (J., 1923, 123, 434) when they attempted to correlate the absorption band of nonyl nitrite with the low-frequency dispersion-constant of a two-term equation *containing only three constants*. Since, however, they also made no correction for the displacement of the head of the absorption-band relative to the real maximum of selective absorption, no important discrepancy was observed, as the two errors are in the same direction. The view set out above receives strong confirmation from the fact that, although the maximum of absorption occurs at exactly the same wave-length in solutions of camphor in benzene and in *cyclo*hexane (J., 1924, 125, 1923), the low-frequency dispersion-constant in the *three*-constant equation for the solution in *cyclo*hexane, $\lambda^2 = 0{\cdot}09114$, $\lambda = 3020$ Å.U., corresponds to a wave-length which is greater by 70 Å.U. than in the case of a *four*-constant equation for the solution in benzene.

(c) *Optical Activity of the Ketonic Group.*—When the experiments now described were begun, we accepted the current view that

Table II.

Rotations of d*-Camphor in Acetone at* 20°.

29·8090 Gms. of camphor in 100 gms. of solution.
Density 0·8405. Length of tube 6 dcm.

$[\alpha] = 0{\cdot}6652\ a.$ $[M] = 1{\cdot}5213\ [\alpha].$

$$[\alpha] = \frac{18{\cdot}022}{\lambda^2 - 0{\cdot}09363} - \frac{7{\cdot}1324}{\lambda^2}.$$

(a) *Visual Readings.*

Wave-length.	Specific rotations. Obs.	Cal.	Diff.
Li 6707·8	34·78°	34·72°	+0·06°
Cd 6438·5	38·98	37·62	+1·36
Zn 6362·3	40·32	40·30	+0·02
Na 5893·0	50·51	50·52	−0·01
Hg 5780·1	53·69	53·60	+0·09
Cu 5782·2	53·57	53·54	+0·03
Cu 5700·2	56·31	55·96	+0·35
Hg 5460·7	64·25	64·20	+0·05
Cu 5218·2	74·61	74·68	−0·07
Ag 5209·1	75·04	75·12	−0·08
Cu 5153·3	77·81	77·84	−0·03
Cu 5105·5	80·33	80·53	−0·20
Cd 5085·8	81·53	80·95	+0·58
Zn 4810·5	99·87	99·98	−0·11
Cd 4799·9	100·68	100·82	−0·14
Zn 4722·2	106·89	107·66	−0·77

(b) *Photographic Readings.*

Wave-length.	Specific rotations. Obs.	Cal.	Diff.
Fe 4982	*86·5°*	*87·9°*	*−1·4°*
4761	*99·8*	*101·1*	*−1·3*
4495	*133·0*	*130·1*	*+2·9*
4397	*146·4*	*143·9*	*+2·5*
4315	*153·0*	*155·5*	*−2·5*
4234	*173·0*	*170·6*	*+2·4*
4165	*184·6*	*182·7*	*−1·9*
4096	*199·6*	*200·6*	*−1·0*
4054	*212·9*	*211·5*	*+1·4*
4005	*226·2*	*225·0*	*−1·2*
3941	*246·0*	*246·1*	*−0·1*

optical activity is a property of the total molecule, and that the picking out of certain atoms as "asymmetric" is merely a convenient way of recording the asymmetry of the molecule as a whole. We have abandoned this view for purely experimental reasons, although in doing so we have taken up an attitude which is more in harmony with modern physical conceptions, since these attribute optical activity to one or more groups each comprising *four pairs of coupled electrons* (Born, *Physikal. Z.*, 1915, **16**, 251; *Ann. Physik*, 1912, [iv], **55**, 177), instead of to an indefinite number of electrons oscillating in spiral paths. Our principal reason for regarding the optical effects as localised is, however, the fact that the dispersion-equations for camphor and its derivatives are haunted by a low-frequency term *the period of which is definitely characteristic of the ketonic group*. We therefore assign this partial rotation to the ketonic group, which is proved to be asymmetric by the unequal yields of the two stereoisomeric products which are obtained when the double bond is converted into two single bonds. This absence of symmetry in a double bond has already been proved in the camphor series by the unsymmetrical reduction of camphor to borneol and *iso*borneol (Montgolfier, *Ann. Chim. Phys.*, 1878, **188**, 5), and of its oxime to bornylamine and neobornylamine (Forster, J., 1898, **73**, 386), and (less directly) by its

TABLE III (*a*).

Rotations of d-*Camphor in* cyclo*Hexane at* 20°.

23·1820 Gms. of camphor in 100 gms. of solution. Density 0·81525. Length of tube 6 dcm.

$[\alpha] = 0{\cdot}8820\ \alpha$. $[M] = 1{\cdot}5213\ [\alpha]$.

$$[\alpha] = \frac{20{\cdot}007}{\lambda^2 - 0{\cdot}09114} - \frac{9{\cdot}2255}{\lambda^2}.$$

Wave-length.	Specific Rotations. Obs.	Cal.	Diff.
Li 6707·8	36·74°	35·38°	$+1{\cdot}3_6$°
Cd 6438·5	39·63	39·58	$+0{\cdot}0_5$
Zn 6362·3	41·04	41·00	$+0{\cdot}0_4$
Na 5893·0	52·25	51·55	$+0{\cdot}7_0$
Hg 5780·1	54·77	54·73	$+0{\cdot}0_4$
Cu 5782·2	55·04	54·68	$+0{\cdot}3_6$
Cu 5700·2	56·53	56·53	±
Ag 5468·6	—	—	—
Hg 5460·7	65·44	65·64	$-0{\cdot}2_0$
Cu 5218·2	76·41	76·56	$-0{\cdot}1_5$
Ag 5209·1	—	—	—
Cu 5153·3	79·38	79·97	$-0{\cdot}5_9$
Cu 5105·6	82·18	81·80	$+0{\cdot}3_8$
Cu 5085·8	83·28	83·77	$-0{\cdot}4_9$
Zn 4810·5	102·58	102·77	$-0{\cdot}1_9$
Cd 4799·9	103·57	103·64	$-0{\cdot}0_7$
Zn 4722·2	109·98	110·33	$-0{\cdot}3_5$
Hg 4358·3	153·65	153·92	$-0{\cdot}2_7$

TABLE III (*b*).

Rotations of Borneol in Benzene at 20°.

22·8550 Gms. of borneol in 100 gms. of solution. Density 0·89903. Length of tube 6 dcm.

$[\alpha] = 0{\cdot}8111\ \alpha$. $[M] = 1{\cdot}5415\ [\alpha]$

$$[\alpha] = \frac{9{\cdot}7866}{\lambda^2 - 0{\cdot}07442} - \frac{3{\cdot}2862}{\lambda^2}.$$

Specific Rotations. Obs.	Cal.	Diff.
18·78°	18·77°	+0·01°
20·95	20·85	+0·10
21·53	21·50	+0·03
26·28	26·48	−0·20
27·93	27·84	+0·09
27·88	28·70	−0·18
29·11	28·95	+0·16
32·62	33·74	−1·12
32·55	32.40	+0·15
37·34	37·39	−0·05
37·47	37·58	−0·11
38·77	38·82	−0·05
39·90	39·94	−0·04
40·32	40·41	−0·09
48·05	48·13	−0·08
48·43	48·48	−0·05
51·28	51·13	+0·15
68·46	67·41	+1·05

TABLE IV.

Rotations of Camphorquinone in Benzene at 20°.

15·069 Gms. of camphorquinone in 100 gms. of solution. Density 0·90290. Length of tube 6 dcm.

$[\alpha] = 1{\cdot}225\ \alpha$. $[M] = 1{\cdot}6611\ [\alpha]$.

$$[\alpha] = -\frac{13{\cdot}170}{\lambda^2 - 0{\cdot}22352}$$

Wave-length.	Specific Rotations. Obs.	Cal.	Diff.
Li 6707·8	− 58·26°	− 58·16°	−0·10°
Cd 6438·5	− 68·60	− 68·93	+0·33
Zn 6362·3	− 72·66	− 72·64	−0·02
Na 5893·0	−105·98	−106·42	+0·44
Cu 5782·2	−117·96	−118·93	+0·97
Hg 5780·1	−118·42	−119·10	+0·68
Cu 5700·2	−128·21	−127·65	−0·56
Ag 5468·6	−174·83	−174·36	−0·47
Hg 5460·7	−176·40	−176·34	−0·06

unsymmetrical bromination to an equilibrium mixture of α- and α′-bromocamphor in the ratio 8 : 1. Since the two links of a double bond in an asymmetric compound are clearly unequal

from the chemical point of view, it would be absurd to pretend that they must be equal from the physical point of view, and no additional justification need therefore be given for using this conception in order to explain the optical properties of camphor or of the other unsaturated compounds now under investigation.

5. *Summary.*

(*a*) The rotatory power of a strong solution of camphor in benzene, for 41 wave-lengths in the visible and ultra-violet regions, can be represented very satisfactorily by the equation

$$[\alpha] = 29{\cdot}384/(\lambda^2 - 0{\cdot}0872) - 20{\cdot}138/(\lambda^2 - 0{\cdot}05428).$$

The low-frequency term corresponds to a wave-length 70 Å.U. greater than the observed "head of the band" at 2880 Å.U. of a film of camphor in benzene and is probably identical with the real maximum of selective absorption. The low-frequency dispersion constant of a three-constant equation for a solution of camphor in *cyclo*hexane shows a further displacement of 70 Å.U., probably as a result of neglecting the high-frequency dispersion-constant, since the maximum of absorption is not displaced by the change of solvent.

(*b*) The rotatory power of borneol in the visible spectrum can be expressed by the equation

$$[\alpha] = 9{\cdot}7866/(\lambda^2 - 0{\cdot}07442) - 3{\cdot}286/\lambda^2.$$

(*c*) The rotatory power of camphorquinone, over the narrow range of transparency in the visible spectrum, can be expressed by the equation

$$[\alpha] = -13{\cdot}170/(\lambda^2 - 0{\cdot}022352),$$

where the dispersion-constant again corresponds with a wave-length, slightly larger (30 to 80 Å.U.) than the observed "head of the band," which is probably identical with the real maximum of selective absorption.

(*d*) The origin of anomalous rotatory dispersion is discussed, and the term "quasi-anomalous" is defined.

We are indebted to the Department of Scientific and Industrial Research for a maintenance grant to one of us (J. O. C.) during the period in which this research was carried out.

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[*Received, February 20th,* 1924.]

XC.—*The Chemistry of the Three-carbon System. Part III. The αβ–βγ Change in Unsaturated Acids.*

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IN the first two papers of this series (J., 1923, **123**, 1361, 2440) it was pointed out that tautomerism, as defined there, occurs in compounds containing a three-carbon system whenever one terminal carbon atom of this system carries a suitable electronegative "activating" group and the two remaining carbon atoms form part of an alicyclic ring or a *gem*-grouping.

$$\begin{matrix}-CH_2\\-CH_2\end{matrix}\!>\!C{:}CHX \qquad\qquad \begin{matrix}-CH_2\\-CH\end{matrix}\!>\!C{\cdot}CH_2X$$

αβ-form. βγ-form.

The cause underlying this phenomenon was thought to be the competition between two opposed factors—the effect of the ring stabilising the βγ-form, and the tendency to produce a conjugated system favouring the αβ-form.

In considering tautomeric systems of this kind—and this applies equally well to keto-enol tautomerism—it is necessary clearly to differentiate between two fundamental properties which characterise them, *viz.*, the degree of mobility of the system and the actual point of equilibrium attained under a given set of conditions. Thus, a system may possess a high degree of mobility and the substance will then occur in one form only, doubtless consisting of an equilibrium mixture containing a large proportion of one individual but reacting in the αβ- or the βγ-form according to circumstances; or both forms may be isolated and be converted one into the other by more or less drastic treatment. *cyclo*Hexenylacetone and ethyl α-cyano*cyclo*hexylideneacetate are good examples of the mobile type (see Part I, *loc. cit.*), whilst the unsaturated acids studied by Fittig supply a classical example of a system which is only mobile in the presence of a powerful reagent; the isomeric αβ- and βγ-acids are otherwise quite distinct and readily separated.

The point of equilibrium, on the other hand, depends only on the relative stability of the two forms and is independent of the rate of conversion. Thus, whilst both the mobile substances mentioned above are only obtainable in one form,* the former has normally the βγ-, the latter the αβ-structure. Again, in Fittig's acids, which are static under ordinary conditions, the equilibrium in the presence of reagents is strongly on the side of the αβ-form,

* It is proposed in the near future to study the possibility of obtaining the two forms of substances of this type.

and this property is so general in the unsaturated acids that it has come to be known as Fittig's rule. The object of the present communication is to examine the point of equilibrium in certain unsaturated acids possessing but a small degree of mobility and therefore particularly suited to our purpose, and to arrive, if possible, at a more trustworthy generalisation.

Up to the present, the principal exception to Fittig's rule was *cyclo*hexylideneacetic acid, which passes completely and irreversibly into its $\beta\gamma$-isomeride on treatment with concentrated alkali (Beesley, Ingold, and Thorpe, J., 1915, **107**, 1081). An explanation of this change has already been suggested, based on the tendency of the double bond to migrate into the ring (Birch, Kon, and Norris, Part I of this series, *loc. cit.*). Some of the cases described by Blaise and Luttringer (*Compt. rend.*, 1905, **140**, 148) might be included under this category, but their acids underwent the $\alpha\beta$–$\beta\gamma$ change under the influence of sulphuric acid, which further transformed the products into lactones and thus removed them from the sphere of the reaction. The same may be said of the acids studied by Fichter, Kiefer, and Bernoulli (*Ber.*, 1909, **42**, 4710), in addition to which it is very doubtful whether the latter authors were dealing with pure materials in all cases (see p. 618).

Some further cases of the $\alpha\beta$–$\beta\gamma$ change have now been studied and we have found that several acids of the general formula (I) will pass into their $\beta\gamma$-isomerides (II) on treatment with alkali; the scheme also applies when the *gem*-dialkyl grouping is replaced

(I.) $\begin{matrix}\mathrm{R{\cdot}CH_2}\\ \mathrm{R{\cdot}CH_2}\end{matrix}\!\!>\!\mathrm{C{:}CH{\cdot}CO_2H}$ $\qquad$ $\begin{matrix}\mathrm{R{\cdot}CH_2}\\ \mathrm{R{\cdot}CH}\end{matrix}\!\!>\!\mathrm{C{\cdot}CH_2{\cdot}CO_2H}$ (II.)

by a *cyclo*hexane or *cyclo*pentane ring. Thus *cyclo*pentylideneacetic acid (III), like its *cyclo*hexane analogue, is very rapidly and completely converted into its isomeride (IV), not only by alkalis,

(III.) $\begin{matrix}\mathrm{CH_2{\cdot}CH_2}\\ \mathrm{CH_2{\cdot}CH_2}\end{matrix}\!\!>\!\mathrm{C{:}CH{\cdot}CO_2H}$ $\qquad$ $\begin{matrix}\mathrm{CH_2{\cdot}CH_2}\\ \mathrm{CH_2{-}CH}\end{matrix}\!\!>\!\mathrm{C{\cdot}CH_2{\cdot}CO_2H}$ (IV.)

but also by mineral acids; it is, in fact, a matter of some difficulty to prepare the pure $\alpha\beta$-acid. However, the chief interest of the present investigation centres on $\beta\beta$-diethylacrylic acid (V) and its isomeride (VI), because these acids have already been studied by Fichter, Kiefer, and Bernoulli (*loc. cit.*).

$\begin{matrix}\mathrm{Et}\\ \mathrm{Et}\end{matrix}\!\!>\!\mathrm{C{:}CH{\cdot}CO_2H}$ (V.) $\qquad$ $\begin{matrix}\mathrm{Et}\\ \mathrm{CHMe}\end{matrix}\!\!>\!\mathrm{C{\cdot}CH_2{\cdot}CO_2H}$ (VI.) $\qquad$ $\begin{matrix}\mathrm{CEt{\cdot}CH_2{\cdot}CO}\\ \mathrm{CHMe{-}\!\!-\!O}\end{matrix}$ (VII.)

These authors describe an acid (b. p. 217—218°; *p*-toluidide, m. p. 95°) to which, from its method of formation, they assigned

the αβ-formula (V). They observed that this acid passed on treatment with sulphuric acid (with or without previous equilibration with alkali) into β-ethylvalerolactone (VII). From this and from a similar observation on the methylethyl acid, they concluded that ββ-dialkylacrylic acids pass into lactones on treatment with sulphuric acid (Fittig's method of separating αβ- from βγ-acids), probably with the intermediate formation of a βγ-acid such as (VI).

The preparation of Fichter's acid by the elimination of water from ethyl β-hydroxy-ββ-diethylpropionate, followed by hydrolysis, was carefully repeated, and an acid giving a *p*-toluidide, m. p. 94°, was readily obtained and further characterised by the preparation of its *amide*, m. p. 113—114°. Its physical and chemical properties, however, did not agree with the constitution assigned to it; on oxidation of its ester with ozone and decomposition of the ozonide with water, acetaldehyde and not diethyl ketone was obtained, showing conclusively that the acid had the βγ-formula (VI). In accordance with this, both the acid and its ester showed a normal molecular refraction.

It appeared certain that Fichter and his collaborators were dealing with the βγ-acid throughout and efforts were made to prepare its isomeride. This was achieved by treating β-hydroxy-ββ-diethylpropionic acid, $Et_2C(OH)\cdot CH_2\cdot CO_2H$, with acetic anhydride, when an unsaturated acid was formed in rather poor yield (mainly owing to the formation of an oily by-product consisting apparently of the *acetyl* derivative of the hydroxy-acid, as it was converted into the latter on hydrolysis with alkali). The new acid proved to be a liquid like its isomeride and had nearly the same boiling point (216°), but it was readily distinguished by the fact that it gave an *amide*, m. p. 89·5°, and a p-*toluidide*, m. p. 80·5°. Its constitution was established by oxidation with permanganate and with ozone (in the form of ester), when diethyl ketone was obtained. In accordance with the αβ-structure (V) assigned to them, both the acid and its ester showed an appreciable exaltation in their molecular refraction. A characteristic difference between the isomeric acids is found in the rate at which they absorb bromine; this also is in keeping with their constitution.

When the carefully purified αβ-acid was treated with boiling alkali for a short time, it was converted apparently completely into the βγ-isomeride. This doubtless accounts for the fact that, although Fichter, Kiefer, and Bernoulli must have actually obtained the ester of the αβ-acid from ethyl α-bromo-ββ-diethylpropionate and diethylaniline, $CHEt_2\cdot CHBr\cdot CO_2Et \longrightarrow CEt_2{:}CH\cdot CO_2Et$, the acid prepared by the hydrolysis of the ester with concentrated alkali was identical with that obtained by their first method, namely,

the βγ-acid. We have found that hydrolysis of the ester with even such a mild reagent as alcoholic sodium ethoxide leads to isomerisation. The αβ-acids are, in general, very sensitive to reagents, and the greatest care is necessary in order to obtain them free from their isomerides. It is for this reason that we did not adopt the method of Harding and Haworth (J., 1909, **95**, 1955), although their product must have consisted mainly of the αβ-acid, as it gave diethyl ketone on oxidation.

The simplest member of the series, ββ-dimethylacrylic acid, could scarcely be expected to undergo the αβ–βγ-change, because the relatively unstable terminal methylene group is known to be formed with difficulty and is sensitive to the action of even mild reagents. Numerous experiments were made on the dehydration of β-hydroxy*iso*valeric acid and its ester, with the object of obtaining the acid $CH_2{:}CMe{\cdot}CH_2{\cdot}CO_2H$, but without success, and it was found that dimethylacrylic acid was quite unaffected by treatment with concentrated alkali. It may, however, be mentioned that the experiments of Bouveault and Wahl (*Compt. rend.*, 1900, **131**, 687), who prepared nitro-derivatives of the βγ- as well as of the αβ-form, point to the potential existence of the former.

It was all the more important for this reason to examine β-methyl-β-ethylacrylic acid (VIII) and its isomeride (IX), which, we found, could be readily prepared by the same general methods.

(VIII.) $\begin{matrix}Me\\Et\end{matrix}\!\!>\!C{:}CH{\cdot}CO_2H$ $\qquad\qquad$ $\begin{matrix}Me\\CHMe\end{matrix}\!\!>\!C{\cdot}CH_2{\cdot}CO_2H$ (IX.)

The αβ-acid was a solid, as described by Fichter and Gisiger (*Ber.*, 1908, **42**, 4707); it gave an *amide*, m. p. 92°, and a p-*toluidide*, m. p. 67°, and yielded methyl ethyl ketone and oxalic acid on oxidation with permanganate; the *ester*, prepared through the acid chloride, showed a marked exaltation of the molecular refraction. The βγ-acid was readily prepared by the usual method and also by boiling the hydroxy-acid with dilute sulphuric acid, although in the latter case a considerable amount of β-methylvalerolactone was formed as well. The acid, which could not be obtained solid at the ordinary temperature, was characterised by the formation of an *amide*, m. p. 123°, and a p-*toluidide*, m. p. 84°; by its oxidation to acetic acid; and by the formation of the ester, which, like the parent acid, showed a normal molecular refraction.

When the pure αβ-acid was treated with concentrated potassium hydroxide under the usual conditions, it underwent conversion to the βγ-acid, although the presence of a small quantity of unchanged acid is not excluded owing to the difficulty of detecting traces of this substance in the presence of its isomeride. There are at present

no trustworthy methods for the separation of such pairs of acids. Fittig's method fails completely, the αβ-acids of this series being converted into lactones like the βγ- (this was first observed by Fichter and his collaborators and confirmed by us, using materials of known purity). It can, however, be stated for the present that the methylethyl acids probably occupy a position intermediate between the diethyl and the dimethyl acids, the equilibrium being still very much on the side of the βγ-forms.

It is proposed in the near future to examine the effect of different substituent groups on the movement of the double bond, and to devise, if possible, more exact methods of estimating the relative stabilities of pairs of unsaturated acids.

EXPERIMENTAL.

Preparation of ββ-Disubstituted Acrylic Acids and their βγ-Isomerides by the Reformatski Reaction.

The method outlined below was found satisfactory in all the cases investigated.

The ketone * (0·75 g.-mol.), ethyl bromoacetate (84 c.c.), and benzene (300 c.c.) are heated with 22 g. of magnesium powder until the reaction begins, efficient cooling with ice-water being then necessary. The reaction product is finally heated for about 15 minutes, decomposed with ice and sulphuric acid, and the benzene solution, after shaking with dilute sulphuric acid, carefully washed with 10% sodium hydroxide. We find this precaution essential in order to obtain a pure and colourless product. The benzene solution is dried, the solvent removed under reduced pressure at as low a temperature as possible (to avoid risk of partial dehydration), and the ester purified by distillation under reduced pressure (yield 60—80%).

For the preparation of the αβ-acid, the hydroxy-ester is hydrolysed with alcoholic potassium hydroxide to the acid, which is then dehydrated with acetic anhydride (Wallach, *Annalen*, 1907, **353**, 288). The βγ-acids are best obtained by digesting the hydroxy-ester with potassium hydrogen sulphate (2 parts) for 3 hours at 160—180° and hydrolysing the resulting ester with alcoholic potassium hydroxide (Wallach, *Annalen*, 1902, **323**, 159).

cyclo*Pentane Series.*

cyclo*Pentanolacetic Acid.*—The acid prepared as above forms large flakes, m. p. 77° after crystallisation from benzene and light petroleum, and is anhydrous (Found: C = 58·41, 58·73; H = 8·33,

* It is advisable to use a 5 to 10% excess of ketone to ensure that all the ethyl bromoacetate is used up.

8·28. Calc., C = 58·29; H = 8·38%), whilst the acid prepared by Harding and Haworth (J., 1910, 97, 486) melted at 76° and is described as a semihydrate; it would appear probable, however, that their product contained some impurity.

*cyclo*Pentylideneacetic acid was obtained in about 60% yield and melted at 63—64°. Δ^1-*cyclo*Penteneacetic acid was prepared as described by Wallach (*Annalen*, 1906, **347**, 324; 1902, **323**, 1521), and melted at 51—52°; a mixture of the two acids melted a little above room temperature.

A solution of *cyclo*pentylideneacetic acid (3 g.) in 45 c.c. of 60% aqueous potassium hydroxide was boiled for 10 minutes. The acid, isolated in the usual manner and recrystallised from light petroleum (2·5 g., m. p. 51°; a further small quantity was recovered from the mother-liquor), was identified as Δ^1-*cyclo*penteneacetic acid by the method of mixed melting points; no trace of the original acid could be isolated from the reaction product.

Diethyl Series.

β-*Ethyl*-Δ^β-*pentenoic Acid* (VI).—The ester, b. p. about 95°/24 mm. or 187—188° at atmospheric pressure, was prepared by dehydrating ethyl β-hydroxy-ββ-diethylpropionate. The acid obtained by hydrolysing it with alcoholic potassium hydroxide had b. p. 133—134°/24 mm. or 217°/763 mm. and formed a colourless, fairly mobile liquid with a faint, disagreeable odour. This did not solidify when cooled to −20°; it had $d_4^{22\cdot7}$ 0·9727; $n_D^{22\cdot7}$ 1·45073; $[R_L]_D$ 35·44 (calc., 35·60).

The *acid chloride*, b. p. 60—61°/14 mm., prepared by the action of thionyl chloride, was a colourless, mobile liquid.

The p-*toluidide*, prepared by the action of the base on the acid chloride or on the acid itself, crystallised from benzene and light petroleum in fine needles (compare Fichter, Kiefer, and Bernoulli, *loc. cit.*), m. p. 94°.

The *amide*, prepared from dry ammonia and the acid chloride in ethereal solution, crystallised well from acetone and light petroleum in plates, m. p. 113—114°, or from benzene and petroleum in needles (Found: C = 66·19; H = 10·19. $C_7H_{13}ON$ requires C = 66·12; H = 10·31%).

The *ethyl* ester, prepared from the pure acid chloride, boiled at 183°/755 mm. and had $d_4^{17\cdot5°}$ 0·9134, $n_D^{17\cdot5°}$ 1·43668, $[R_L]_D$ 44·75 (calc., 44·95). A chloroform solution of the pure ethyl ester was oxidised with ozonised oxygen; 3 g. required nearly 60 hours for complete oxidation. After removal of the solvent, the ozonide was decomposed with warm water in a current of carbon dioxide, the gases being led through a solution of β-naphthol in acetic acid containing

hydrochloric acid. The latter solution was then warmed for ½ hour, cooled, and diluted, when the characteristic ethylidene-β-dinaphthyl oxide, m. p. 170—172°, separated, accompanied by the corresponding acetal, m. p. 200—201°; the yield of these two products, which were compared with specimens prepared from acetaldehyde, corresponded with an almost theoretical yield of acetaldehyde from the ozonide. The residue in the flask gave a deep red colour with alcoholic ferric chloride and presumably contained ethyl propionylacetate.

β-Ethyl-Δ^{β}-pentenoic acid readily absorbs two atoms of bromine in acetic acid solution to form an oily *dibromide* which could not be purified.

On boiling the acid with 50% (by volume) sulphuric acid for 15 minutes, a 60% yield of β-ethylvalerolactone, b. p. 226°, was obtained, although the yield was only 10% after 5 minutes.

ββ-*Diethylacrylic acid* (β-*ethyl*-Δ^{α}-*pentenoic acid*) was prepared from the corresponding hydroxy-acid in about 50% yield and boiled at 129°/23 mm. as a colourless liquid with a faint pungent smell; it had $d_4^{21\cdot2^\circ}$ 0·9682, $n_D^{21\cdot2^\circ}$ 1·46270, $[R_L]_D$ 36·42 (calc., 35·60) (Found: C = 65·30; H = 9·34. $C_7H_{12}O_2$ requires C = 65·59; H = 9·45%).

The *acid chloride* boiled at 85°/25 mm. The p-*toluidide* crystallised well from benzene and light petroleum, forming large needles, m. p. 80·5°; a mixture of this compound with the βγ-isomeride melted below 70° (Found: C = 77·31; H = 8·99. $C_{14}H_{19}ON$ requires C = 77·35; H = 8·81%).

The *amide* was much more soluble in acetone than its isomeride, but crystallised well from ether and light petroleum or benzene and light petroleum, forming long needles, m. p. 89° (Found: C = 66·33; H = 10·38. $C_7H_{13}ON$ requires C = 66·72; H = 10·31%).

The *ethyl* ester, prepared from the acid chloride, boiled at 87—88°/23 mm., 187—188°/755 mm., and had $d_4^{16\cdot6^\circ}$ 0·90955, $n_D^{16\cdot6^\circ}$ 1·44542, $[R_L]_D$ 45·72 (calc., 44·95) (Found: C = 68·60; H = 10·17. $C_9H_{16}O_2$ requires C = 69·18; H = 10·32%).

The pure acid was oxidised with alkaline potassium permanganate, and the product distilled in steam, when a quantity of diethyl ketone was obtained (identified as the semicarbazone, m. p. 135°); the residue in the flask contained oxalic acid. The same products were also obtained by oxidising the ester with ozone; the oxidation was much slower and less complete than in the case of the isomeric acid. The αβ-acid reacted very incompletely with bromine, only about 25% of the theoretical amount being absorbed in the cold. A solid bromide could not be isolated.

The action of sulphuric acid on the αβ-acid, on the other hand, proceeded exactly as in the case of the βγ-acid, a yield of about 60% of the same lactone being produced in 15 minutes.

ββ-*Diethylacrylic acid* was treated with 60% potassium hydroxide exactly as described in the case of *cyclo*pentylideneacetic acid (p. 621), the mixture being allowed to boil for 20 minutes. The acid isolated had $d_4^{21\cdot7^\circ}$ 0·9629, $n_D^{21\cdot7^\circ}$ 1·45223, $[R_L]_D$ 35·90, thus showing that a considerable amount of conversion to the βγ-isomeride had taken place. It was then converted through the acid chloride into the amide, which melted at 107° after one crystallisation; no trace of the isomeric amide, m. p. 89°, could be isolated. The experiment was repeated, starting with the pure βγ-acid; the product showed $d_4^{19\cdot1^\circ}$ 0·9644, $n_D^{19\cdot1^\circ}$ 1·45183, $[R_L]_D$ 35·82 and the amide prepared from it melted at 114° after one crystallisation. It follows, therefore, that the point of equilibrium is very much on the side of the βγ-acid.

Methylethyl Series.

β-*Methyl*-Δ^{β}-*pentenoic Acid* (IX).—This acid, b. p. 116°/23 mm., was prepared by the standard method or by dehydrating the hydroxy-acid with 12% sulphuric acid. When anhydrous formic acid was used in place of sulphuric acid as dehydrating agent, the product contained about 30% of the isomeric αβ-acid. The acid had $d_4^{23\cdot2^\circ}$ 0·97845, $n_D^{23\cdot2^\circ}$ 1·44692, $[R_L]_D$ 31·15 (calc., 30·98).

The *acid chloride* boiled at 57°/25 mm. The p-*toluidide* crystallised from light petroleum containing a little benzene in fine needles, m. p. 84° (Found: C = 76·70; H = 8·49. $C_{13}H_{17}ON$ requires C = 76·79; H = 8·43%). The *amide* separated from benzene and light petroleum in silvery plates, m. p. 123—124°. The *ethyl* ester boiled at 62°/13 mm. and had $d_4^{18\cdot8^\circ}$ 0·91633, $n_D^{18\cdot8^\circ}$ 1·43638, $[R_L]_D$ 40·58 (calc., 40·33).

The acid was oxidised with alkaline potassium permanganate, when acetic acid was isolated; no trace of oxalic acid was produced. The ester was oxidised with ozone and the ozonide decomposed with water, a good yield of acetaldehyde being obtained.

β-*Methyl*-β-*ethylacrylic Acid* (β-*methyl*-Δ^{α}-*pentenoic acid*).—This acid was produced in 34% yield from the hydroxy-acid; it boiled at 121—122°/22 mm., solidified on cooling, and formed flattened needles, m. p. 45°, when recrystallised from light petroleum.

The *acid chloride* boiled at 65°/25 mm. The p-*toluidide* formed needles from benzene and light petroleum or plates from ether and light petroleum, m. p. 66—67°; a mixture of this substance with its isomeride, m. p. 84°, melted at about 52° (Found: C = 77·09; H = 8·53. $C_{13}H_{17}ON$ requires C = 76·79; H = 8·43%). The *amide* crystallised from benzene and light petroleum in plates,

m. p. 92—93°; a mixture of this compound with the βγ-isomeride melted at about 70° (Found: C = 64·04; H = 9·71. $C_6H_{11}ON$ requires C = 63·60; H = 9·78%). The *ethyl* ester boiled at 67°/24 mm. and had $d_{4°}^{17·9°}$ 0·91413, $n_D^{17·9°}$ 1·44110, $[R_L]_D$ 41·06 (calc., 40·33).

Both the acid and the ester were oxidised and gave methyl ethyl ketone (*p*-nitrophenylhydrazone, m. p. 126°) and oxalic acid.

The acid was treated with potassium hydroxide under the same conditions as the diethyl acid (p. 621). The acid isolated was a liquid, b. p. 113—115°/23 mm., $d_{4°}^{23·1°}$ 0·97772, $n_D^{23·1°}$ 1·44753, $[R_L]_D$ 31·21; the amide prepared from it melted at 119—120° in the crude state and at 123—124° after one crystallisation. In another experiment the acid after treatment with potassium hydroxide was characterised by means of the p-*toluidide*, which melted at 84° after one crystallisation. The βγ-acid was treated with alkali in the same way. The product gave an amide melting in the crude state at 90—95°, at 117° after one crystallisation. The amount of conversion to the αβ-acid was therefore very small, but possibly somewhat greater than in the case of the higher homologue.

Dimethyl Series.

The condensation of acetone with ethyl bromoacetate in benzene solution in presence of magnesium does not proceed easily, there being an "induction period" of about 3 days; once started, the reaction is very vigorous. The hydroxy-ester, b. p. 88—89°/19 mm., is obtained in a yield of about 40%. All the methods of dehydrating the hydroxy-ester or the acid led to ββ-dimethylacrylic acid, which was identified in the usual way. This acid was quite unaffected by boiling with 60% aqueous potassium hydroxide for ½ hour.

The authors have to acknowledge their indebtedness to the Chemical Society for a grant which has partly defrayed the cost of this investigation.

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SOUTH KENSINGTON, S.W. [*Received, December 19th*, 1924.]

XCI.—*A Method of Determining the Presence or Absence of Complex Salts or Ions in Dilute Aqueous Solution.*

By WILLIAM HAMILTON PATTERSON and JOHN DUCKETT.

THE temperature of mutual miscibility of two liquids is in general markedly altered by the addition of even small quantities of other components.

The following experiments were carried out with phenol (36·1%) and water (63·9%), proportions which, even with slight variation, give the critical solution temperature of 66·0° (temperature of critical turbidity). The added substances were inorganic salts, or mixtures of two salts, the object in the latter case being to test whether or not the two existed independently in solution.

Symbols similar to those of Timmermans (*Z. physikal. Chem.*, 1907, **58**, 129) have been adopted: C = concentration of salt per 1000 g. of total solution (phenol + water + salt). Mol. C = molecular concentration. e = elevation of critical solution temperature. E = molecular elevation = e/mol. C.

From the values of E or e conclusions can be drawn as to the condition of the salts in dilute aqueous solution, in this case above 66° (when the proportions of phenol and water given above are used).

These conclusions are based on the following observations — The simpler inorganic salts are soluble in the aqueous phase only and therefore greatly raise the critical solution temperature. In a previous communication (*J. Physical Chem.*) we have shown that the increase of critical solution temperature caused by the addition of various salts is the sum of the ionic values, and that the anions and kations may be arranged, in this respect, in a series almost identical with the Hofmeister series (for the coagulation of neutral egg-albumin).

Further, valency has a great effect on the critical solution temperature, the substitution of a bivalent for a univalent ion producing a much greater increase than that of a tervalent for a bivalent ion. Hence the more complex the molecule the greater the rise obtained on dissolving equimolecular quantities; *e.g.*, the addition of 0·03 mol. of the salts named gives the following values of e: KCl 2·95°, NaCl 3·75°, K_2SO_4 7·95°, Na_2SO_4 9·7°, $MgSO_4$ 10·75°, $Cr_2(SO_4)_3$ 15·0°.

Curves showing the relation between e, or E, and mol. C have been plotted for a number of salts. The former curves (see Fig. 1), after an initial bend at low concentration, approach a straight line, so that intra- or even extra-polation can be made within the limits of experimental error (temperatures being measured to 0·05°).

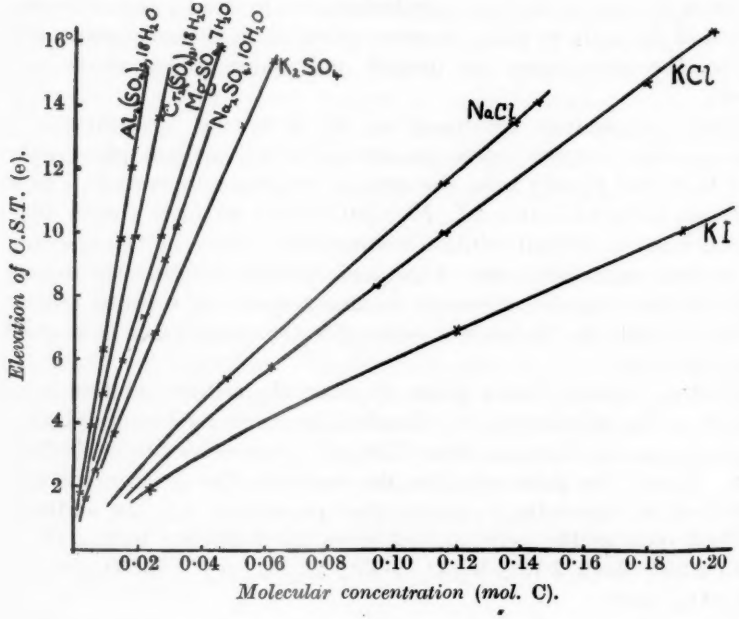
For salt pairs, additive values of e imply that neither complexes nor double molecules exist in the solution. Deviations from the separately calculated values measure the molecular complexity.

Simple Mixtures.

Lithium chloride, mol. C 0·1141, + *potassium chloride*, mol. C 0·1131. e (observed for mixture) 18·6°.

In this, and every other case, the rise calculated from the values for the components agrees best with that found experimentally (for the mixture) when the mean for the double concentration of each separately is chosen: *e.g.*, *e* for 0·2282 mol. *C* of LiCl (from the curve) = 19·75°, and for 0·2263 mol. *C* of KCl, 17·50°; mean 18·63°. Simply to add together the values of *e* for each salt is to ignore the presence of the other salt already in solution and results in a slight deviation from the experimental value. The above method of calculation has therefore been adopted throughout.

FIG. 1.



Sodium chloride, mol. *C* 0·1047, + *potassium chloride*, mol. *C* 0·1047.

The calculated and the experimental value of *e* agree, 18·4°.

This result, provided the temperature difference affords no explanation, is not in harmony with the theory of Braley and Hall (*J. Amer. Chem. Soc.*, 1920, **42**, 1770), who account for the transference numbers of sodium and potassium in mixed chloride solutions at 25° by postulating the existence of complexes,

$$NaCl + KCl \rightleftharpoons Na(KCl_2) \rightleftharpoons Na^{\cdot} + KCl_2'\,;$$

an argument made use of in favour of progressive ionisation of strong electrolytes with increasing dilution.

$MgSO_4 + KCl$.

	Mol. *C*.	*e* calc.	Mean calc.	*e* obs.
$MgSO_4$	0·0211	14·51°	9·3°	9·9°
KCl	,,	4·03		
$MgSO_4$	0·0324	21·7	13·8	13·9
KCl	,,	5·92		

$K_2SO_4 + MgSO_4$.

	Mol. *C*.	*e* calc.	Mean calc.	*e* obs.
K_2SO_4	0·0138	7·38°	8·7°	8·75°
$MgSO_4$	,,	9·98		
K_2SO_4	0·0293	14·23	16·9	17·8
$MgSO_4$	,,	19·61		

$Na_2SO_4 + MgSO_4$.

Na_2SO_4	0·00666	4·42°	5·0°	5·7°
$MgSO_4$	,,	5·50		
Na_2SO_4	0·01045	6·90	7·4	7·7
$MgSO_4$	,,	7·95		
Na_2SO_4	0·0166	10·42°	11·0°	10·7°
$MgSO_4$	,,	11·61		
Na_2SO_4	0·0218	13·6	14·2	14·2
$MgSO_4$	,,	14·9		

Potassium alum.

Mol. *C*. (as double mol.). $\times 10^5$.	*e* calc. for double *C* of each salt component. K_2SO_4.	$Al_2(SO_4)_3$.	*e* calc. Mean.	*e* obs.
3·49	2·1°	4·8°	3·5°	3·8°
7·63	4·43	10·1	8·4	8·2
17·63	5·1	11·6	11·9	11·8
18·26	9·25	24·2	16·7	15·4
22·75	11·2	30·0	20·6	19·0

Chrome alum.

Mol. *C*. (as double mol.). $\times 10^5$.	*e* calc. for double *C* of each salt component. K_2SO_4.	$Cr_2(SO_4)_3$.	*e* calc. Mean.	*e* obs.
2·2	1·5°	2·8°	2·2°	2·2°
7·1	4·15	7·3	5·8	5·8
16·0	8·40	15·62	12·0	11·6
24·7	12·1	23·4	17·8	17·2

Iron Alum.—The curve for iron alum lies just below that of potassium alum, and the result, by analogy, may be taken as similar.

The small deviation for the higher concentrations in the case of potassium alum may imply a tendency to form double molecules (the ordinary alum molecule) with increasing concentration, in spite of the higher temperature; the number formed, however, must be relatively small.

A series of separate experiments up to 47·5° with a phenol–water mixture having a temperature of mutual miscibility 34·8° indicated appreciable formation of the alum molecule. Errors due to hydrolysis of aluminium sulphate, chemical reaction with phenol, etc., may be expected to compensate in the case of simple mixture.

Complex Formation.

The trustworthiness of the method was tested by selecting cases where complex formation might be expected to occur.

Sodium Ferrocyanide.—The curve (plotted for the normal molecular weight) lies just above that of aluminium sulphate. The following figures are normal and indicate no change of condition of the salt in solution.

C	Mol. *C*.	C.S.T.	*e*.	*E*.
2·682	0·0055	70·75°	4·75°	857°
4·220	0·0087	72·9	6·9	791
5·765	0·0119	74·85	8·85	743
7·913	0·0164	77·8	11·8	722

Sodium cyanide, mol. C 0·0094—0·0224, produces the largest lowering of critical solution temperature found for any substance, E — 1559 to — 1192. The curve bends, indicating probably the extent of hydrolysis.

Sodium Ferrioxalate.—The curve is nearly identical with that of chromic sulphate. Mol. C 0·0152—0·036. $E = 552$—493. Sodium oxalate, mol. C 0·066—0·093. $E = 273$—210.

Even in saturated sodium sulphate solution, both sodium ferrocyanide and sodium ferrioxalate must be strongly ionised (compare Turner and Patterson, *Trans. Faraday Soc.*, 1924, **20**, 345); a part of the ions must therefore be complex.

Mercuric Iodide + Potassium Iodide.—

	Mol. C.	e.	E.	
HgI_2	0·0043	0·2°	46·6°	(limit of solubility)
KI	0·0250	1·85	74·0	
	0·1215	6·95	57·7	
	0·193	10·15	52·7	
	0·347	17·1	49·4	
Equimolecular mixture	0·0616 of each	−9·1	−74	

These results indicate combination between the molecules and also that the complex is appreciably soluble in phenol.

Cadmium Iodide.—Mol. C 0·0106. $e = 0·7°$. The value of e remains the same as mol. C increases to 0·049; this can only be due to increasing complexity. The value for $Cd^{\cdot\cdot}$ (ion) obtained from cadmium chloride or sulphate is normal; Cd = 2 Na (approx.).

Cadmium Iodide + Potassium Iodide.—On adding a molecular equivalent of potassium iodide to cadmium iodide, e became 1·10°, a rise of only 0·4°, instead of the 3·4° to be expected if only simple mixture had occurred. Complex formation may thus be supposed to occur to the extent denoted by the ratio (3·4—0·4)/3·4.

In conclusion, the authors desire to express their thanks to Messrs. J. H. Carrington and L. R. Hickson for making the experiments with lithium chloride and for repeating several of the determinations.

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[*Received, December 12th*, 1924.]

XCII.—*Studies on Starch. Part II. The Constitution of Polymerised Amylose, Amylopectin, and their Derivatives.*

By Arthur Robert Ling and Dinshaw Rattonji Nanji.

A continuation of our experiments (J., 1923, **123**, 2666) has led to results which have enabled us to draw definite conclusions on the subject as well as to reconcile our work with that of others.

Some misconception has arisen with regard to the quantity of amylose and amylopectin in starch granules. Thus Samec and Höft (*Koll. Chem. Beihefte*, 1913, **5**, 141) assert that starch contains 17% of "amylose" and 83% of amylopectin. Pringsheim and Wolfsohn (*Ber.*, 1924, **57**, [*B*], 887), who prepared "amylose" by one of our methods (*loc. cit.*, p. 2673), were able to obtain only 14% from anhydrous starch. They therefore accept the views of Samec and Höft, in spite of the fact that they were not able to obtain more than 28% of amylopectin from starch. We shall show that in those starches which contain "amylose" and amylopectin only, these substances are present to the extent of 66·6 and 33·3%, respectively. The explanation of the discrepancies is that "amylose" as it exists in starch granules is present in more than one physical state and possibly in different degrees of hydration. From an histological investigation of starch granules, an account of which will be published elsewhere, we find that about 25% of the "amylose" exists as a crystalloidal phase in the form of spherites constituting a core round the hilum of the granule. This portion is readily extracted by water or by dilute alkali. The remainder, which presents a colloidal phase, is dispersed uniformly in the amylopectin layers. It appears to exist either as a solid solution or to be so strongly adsorbed on the amylopectin as to resist extraction. It is, however, quite possible to remove the whole of the amylose from starch paste by treating the latter with barley diastase at 50°, whereby the amylose is converted into maltose and the amylopectin into αβ-hexa-amylose. Ling, Nanji, and Harper (*J. Inst. Brewing*, 1924, **30**, 838) have utilised these facts in a method of estimating "amylose" and amylopectin in barley and wheat.

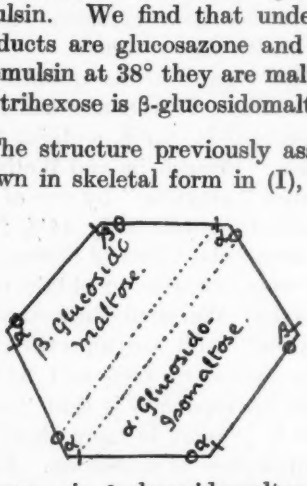
When a solution of amylose is treated with a minute quantity of barley or malt diastase at p_H 4·5, it is converted rapidly into maltose, the optimum temperature being between 30° and 40° for the former and 45° for the latter. At 70°, scarcely any action occurs. No intermediate sugar is formed as in the case of αβ-hexa-amylose.

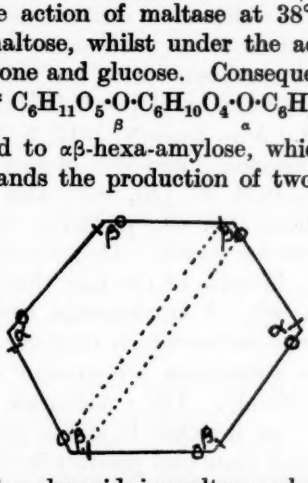
Since Neuberg and Saneyoshi (*Biochem. Z.*, 1911, **34**, 44; *Z. Ver.*

deut. Zuckerind., 1912, 559) have shown that the osazones of the bioses are capable of being hydrolysed by enzymes, this afforded a means of establishing the constitution of the trihexose derived from amylopectin which, as previously stated (*loc. cit.*), may be either β-glucosidomaltose or α-glucosido*iso*maltose. To decide between these alternatives, we have studied the products of hydrolysis of the osazone of the trihexose by the α- and β-enzymes, maltase and emulsin. We find that under the action of maltase at 38° the products are glucosazone and *iso*maltose, whilst under the action of emulsin at 38° they are maltosazone and glucose. Consequently the trihexose is β-glucosidomaltose,* $C_6H_{11}O_5 \cdot O \cdot C_6H_{10}O_4 \cdot O \cdot C_6H_{10}O_5$ (β, α).

The structure previously assigned to αβ-hexa-amylose, which is shown in skeletal form in (I), demands the production of two tri-

(I.)





(II.)

hexoses, *viz*, β-glucosidomaltose and α-glucosido*iso*maltose, whereas the product obtained by the action of malt diastase at 70° on amylopectin and consequently on αβ-hexa-amylose consists, as shown above, exclusively of β-glucosidomaltose. The structure I requires therefore some modification to accommodate this fact. If one of the trihexose halves in the αβ-hexa-amylose, *viz.*, that representing α-glucosido*iso*maltose, be turned through 180°, a structure is obtained which can yield on hydrolysis entirely β-gluco-

* In Part I, the constitution of the *iso*maltose unit was provisionally put forward as 1 : 5-glucosidoglucose. The precise constitution of this disaccharide is at present *sub judice*, and this together with Haworth's observation, that cellobiose is 1 : 5-glucosidoglucose, leads us to the view that the precise constitution of *iso*maltose should be left open for the present. This much, however, we may state. The β-linkings used throughout the papers to represent the *iso*maltose unit may either be 1 : 5 or 1 : 4, and the oxidic ring, butylene- or amylene-oxide respectively. Both these alternatives account for the production of 2 : 3 : 6-trimethyl glucose from starch (Irvine and Macdonald, J., 1924, **125**, 942). Even if 2 : 3 : 6-trimethyl glucose is not obtained from isolated *iso*maltose, the possibility is not excluded that there may be a shifting of the amylene-oxide ring in αβ-hexa-amylose on its hydrolysis with enzymes or acids to a hexylene-oxide ring, just as in the hydrolysis of sucrose an amylene-oxide ring passes into a butylene-oxide ring (Haworth and co-workers, J., 1923, **123**, 294).

sidomaltose. But the linkings of the two β-glucosidomaltose units present three possibilities. They may be both α-linkings, one may be an α- and the other a β-linking, or both may be β-linkings. When we come to consider the nature of the so-called stable dextrin (see Part III), it will be seen that preference must be given to formula (II) as representing the constitution of αβ-hexa-amylose.

Throughout the work the exploring agents employed were exclusively enzymes, and by their aid we have not only realised quantitative yields of hydrolytic products, but have been able to assure ourselves that no secondary changes occurred. It seems, therefore, at first sight surprising that our conclusions should conflict with those of Irvine, Pringsheim, and Macdonald (J., 1924, **125**, 942) on the molecular structure of αβ-hexa-amylose. The differences in our views would seem, however, to be apparent rather than real. But there are fundamental differences in the way in which the problem has been attacked by the chemists just mentioned and by ourselves. In the first place, Irvine, Pringsheim, and Macdonald worked on β-hexa-amylose obtained from one of the products of the action of *Bacillus macerans* on starch. As the parent substances thus formed—the crystalline "dextrins" of Schardinger—are products of the metabolism of an organism, their relation to the constituents of starch itself is uncertain. In any event they do not exist as such among the integral constituents of starch granules. Secondly, the chemical treatment, methylation, to which the β-hexa-amylose was subjected is open to criticism, as there is reason to believe from the evidence furnished by the authors themselves that secondary changes occurred, whilst the yield of trimethylamylose was only 29% of the theoretical. Its product of hydrolysis was 2 : 3 : 6-trimethyl glucose, a fact which may indicate its relation to our αβ-hexa-amylose. Indeed, in our previous paper (*loc. cit.*, p. 2669), we put forward the view that Pringsheim's β-series of amyloses belongs to the same series as our αβ-hexa-amylose. That being so, the absence of 2 : 3 : 5-trimethyl glucose at which Irvine, Pringsheim, and Macdonald express surprise must be due, as previously suggested, to steric hindrance. The major portion of the product obtained by the methylation of β-hexa-amylose consisted (apart from substances due to secondary changes) of derivatives, the methoxyl content of which was below that required for a trimethylamylose.*

* In a footnote to the paper by Irvine, Pringsheim, and Macdonald (*loc. cit.*, p. 943) it is stated that opportunity is taken to *correct* certain statements made by us in the previous paper that "*in establishing the constitution of such closed-chain compounds* (*amylose*) *a very important factor presents itself which has been left out of consideration, namely, that of steric hindrance.*" None of

EXPERIMENTAL.

Hydrolysis of α-Hexa-amylose with the Diastase from Malt and Barley.

Velocity of Hydrolysis of "Amylose" with Malt Diastase at Different Temperatures.—Four 100 c.c. portions of a 1% solution of amylose brought to p_H 4·5 were treated at 30°, 40°, 50°, and 70° with a solution containing 2 mg. of precipitated malt diastase, and these portions were kept at the respective temperature for 5 minutes, the reaction being then arrested by the addition of a drop of 10% caustic soda solution. The liquids were then made up to 200 c.c. and titrated against 5 c.c. of Fehling's solution. The results are shown in the following table (a = percentage of amylose hydrolysed in 5 minutes), from which it will be seen that the optimum temperature lies between 30° and 40°.

Temp.	30°	40°	50°	70°
a.	97·2	98·7	78·3	15·1
Iodine coloration	nil	nil	very feeble	deep blue

The remaining portions of the solutions representing the conversions carried out at 30° and 40° were combined and concentrated to a small volume. The dissolved matter was completely fermentable with yeast and gave maltosazone. The sugar was therefore maltose.

Hydrolysis of α-Hexa-amylose at 70° with Malt Diastase Previously Heated to the Same Temperature.—Malt diastase solution which had been previously heated at 70° for ½ hour was practically without action on "amylose" even after incubating at 70° for 2 hours. With malt-diastase solution previously heated for a shorter period

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the fresh arguments brought forward by the authors contradicts our statement and therefore we fail to see the necessity for any "correction."

We must still maintain that the conception of steric hindrance and its connexion with carbon atom 5 have never been alluded to directly in any paper dealing with constitutional studies on the *polysaccharides* published prior to our paper. We may ask the question—If the effect of steric hindrance at position 5 were so well known, why was the presence of 2 : 3 : 5-trimethyl glucose vainly sought for among the products of hydrolysis of methylated starch, and why were all those considerations which involved the formation of this trimethyl glucose finally rejected? To quote Irvine's words at the meeting of the British Association (1922)—when he rejected Karrer's formula for his diamylose on exactly the above grounds—"*The only trimethyl glucose to which such a structure could give rise is the* 2 : 3 : 5*-form described by Irvine and Oldham*" (J., 1921, **119**, 1744). He proceeds: "*No trace of this compound was detected by us, and moreover the* 2 : 3 : 6*-variety of trimethyl glucose actually obtained cannot possibly be accommodated by Karrer's formula.*" In the light of our own work the 2 : 3 : 6-variety must therefore have been obtained from the amylopectin portion of the rice starch employed by Irvine, which cannot be regarded as a chemical entity, containing as it does three distinct substances.

at 70°, the percentage of amylose hydrolysed was exceedingly low. The sugar formed under these conditions was identified as maltose.

Velocity of Hydrolysis of α-Hexa-amylose with Barley Diastase at Different Temperatures.—Four 100 c.c. portions of a 1% solution of the " amylose " at p_H 4·5 were raised to 30°, 40°, 45°, and 50°, respectively, and treated at these temperatures for 5 minutes with 2 c.c. of barley diastase solution (equivalent to 2 g. of barley). The reducing powers were then determined as in the case of the similar experiments with malt diastase. The results are as follows :

Temp.	30°	40°	45°	50°
% Maltose produced	38·0	44·9	55·3	53·2
% " Amylose " hydrolysed	36·0	42·5	52·4	50·4

A 2% solution of the amylose (100 c.c.) was treated with 5 c.c. of a solution of barley diastase (equivalent to 5 g. of barley) for 3 hours, when it no longer gave a coloration with iodine. The constants of the solution were $[\alpha]_D$ 137·8° and R 98·7, substantially those of maltose, and it was proved to consist exclusively of maltose.

Relative Quantities of α-Hexa-amylose and of αβ-Hexa-amylose in Different Starches.

When a starch paste is treated with barley diastase at a convenient temperature, say 50°, the " amylose," being completely converted into maltose, may be measured by the reducing power. The percentage of maltose thus formed may be converted into amylose by the factor 0·947, the percentage of amylopectin being the difference between 100 and the percentage of " amylose." The results of the estimation of " amylose " and amylopectin in different starches are given below.

Starches.	Percentage of " Amylose."	Percentage of Amylopectin.
Arrowroot	65·8	34·2
Potato	67·2	32·8
Wheat	66·3	33·7
Barley	68·2	31·8
Rice	66·2	33·8

It should be pointed out that the values given in the table for the percentages of " amylose " and amylopectin in the case of the starches of barley, wheat, and rice are only relative, and that the actual percentages of " amylose " and amylopectin calculated on these starches would be considerably lower depending on their hemicellulose content, which may vary between 8 and 18%, or in some cases, maize for example, it may be less. In these starches a part of the hemicellulose is intimately associated with the granules, forming, in fact, an integral portion of them, and therefore it cannot be separated by any physical means. The other portion of the

hemicellulose is derived from the cell wall and it is present to a greater or less extent according to the degree of fractionation to which the starch has been subjected in its manufacture. When a paste from any of the starches is treated with barley diastase at about the optimum temperature, the " amylose " is, as we have seen, converted into maltose, the amylopectin is dephosphated and depolymerised, whilst the hemicellulose is left unaltered and may be filtered off from the soluble products.

It may be pointed out that, provided the barley diastase is freshly prepared from a barley which is sound and has undergone no modification during harvesting or storage, no abnormalities in its chemical activity need be feared.

Hydrolysis of the Trihexosazone with Maltase.—A solution of the osazone (0·8 g.) in hot water was cooled to 38° and a cold water extract of dried yeast corresponding with about 3 g. of the yeast added. After the addition of a little toluene the mixture was incubated at 38° for 96 hours, within which time the hydrolysis was practically complete. After about 48 hours, the liquid became cloudy and subsequently turbid. Finally, when the liquid was cooled in an ice-chest, a precipitate separated which was identified as glucosazone by its crystalline form and melting point (201°). Since part of the osazone remained dissolved, it was not possible to estimate the yield.

The filtrate from the glucosazone was acidified with a few drops of acetic acid and heated with a small quantity of norit, which removed the glucosazone. The liquid without filtering was made up to 100 c.c. and filtered. The reducing power of the filtrate was equal to 0·31 g. of maltose or 0·38 g. of *iso*maltose per 100 c.c. Theoretically 0·8 g. of the triosazone should yield 0·4 g. of a disaccharide.

The portion of the filtrate remaining after the determination of the reducing power was divided into two parts. One part was concentrated on a water-bath to a small volume and heated with phenylhydrazine acetate in the usual manner. The osazone which separated after about 12 hours was *iso*maltosazone; it melted at 145°. Twenty-five c.c. of the filtrate were incubated with emulsin in presence of a little toluene for 24 hours, a blank experiment with emulsin being carried out under the same conditions. The solution was then diluted to 50 c.c., and its reducing power determined; the latter corresponded with 0·32 g. of *iso*maltose per 100 c.c. instead of 0·19 g., the value before the action of the emulsin.

Hydrolysis of the Trihexosazone with Emulsin.—A solution of 0·8 g. of the osazone in hot water was cooled to 38° and incubated at that temperature with a solution of emulsin corresponding

with 5 g. of bitter almonds in presence of a little toluene for 96 hours.

Slight resinification occurred during the incubation unless air was excluded. To overcome this difficulty, a narrow-necked flask was filled to the neck with the solution, the surface of which was then covered with a layer of toluene, and the flask closed with a cork. After being incubated for 96 hours at 38°, the osazone solution showed no turbidity. After keeping at the room temperature for about 12 hours, a small quantity of minute, yellow crystals having the characteristic appearance under the microscope of maltosazone separated; m. p. 188° (maltosazone when not quite pure melts at about this temperature). The quantity obtained was not sufficient for recrystallisation, but we have no doubt whatever that the substance was maltosazone. The filtrate was acidified with a few drops of acetic acid and gently warmed with a little norit. It was cooled and made up to 100 c.c.; the reducing power of the filtrate corresponded with 0·19 g. of glucose per 100 c.c. instead of 0·22 g., the theoretical quantity. The remainder of the filtrate was concentrated to a small volume and heated with phenylhydrazine acetate in the usual manner. After a short time, a yellow, crystalline precipitate separated which was identified as glucosazone by its crystalline form and melting point.

Comparative Velocity of Hydrolysis of α- and β-Linkings.—To investigate this point, maltase and emulsin were allowed to act on maltose, and on *iso*maltose and the trihexose.

Experiments with maltase. Two solutions were prepared, one containing 2 g. of anhydrous maltose, and the other 3 g. of β-glucosidomaltose. To each was added the same quantity of a solution containing yeast maltase. Both solutions were then made up to 200 c.c. and after the addition of a trace of toluene they were incubated at 38°, portions being withdrawn at different intervals and the reducing powers determined. From the increase in the reducing powers, the percentage of α-linking hydrolysed could be calculated.

Experiments with emulsin. These experiments were carried out on the same lines as those in which maltase was used, but the substrates were *iso*maltose and β-glucosidomaltose.

The results of both series are given in the following table:

Substrate.	Maltose.	β-Glucosido-maltose.	*iso*Maltose.	β-Glucosido-maltose.
Time (hrs.).	% of α-linking hydrolysed.	% of α-linking hydrolysed.	% of β-linking hydrolysed.	% of β-linking hydrolysed.
1	32·6	30·1	28·2	24·6
2	58·1	55·8	52·5	45·0
4	72·3	68·7	65·8	57·9
6	82·5	76·4	75·1	66·4
24	99·2	93·6	98·6	92·0

It is seen from these results that whilst there is no essential difference in the action of the two enzymes on maltose, *iso*maltose, and the trihexose, the velocity of hydrolysis is sensibly greater in the case of the two bioses than in that of the triose.

The expenses connected with these investigations have been partly defrayed by a grant from the Government Grant Committee of the Royal Society, to whom our thanks are due. We have also to express our thanks to Mr. W. J. Harper for carrying out much of the analytical work herein described.

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XCIII.—*Studies on Starch. Part III. The Nature and the Genesis of the Stable Dextrin and of the Maltodextrins.*

By Arthur Robert Ling and Dinshaw Rattonji Nanji.

It has been shown (preceding paper) that α-hexa-amylose is converted quantitatively into maltose by barley or malt diastase at 50° without the production of any intermediate substances, whereas αβ-hexa-amylose under the action of malt diastase at 70° yields β-glucosidomaltose, *iso*maltose, maltose, and glucose according to the conditions. We shall now show that αβ-hexa-amylose, when treated with malt diastase between 30° and 70° in presence and in absence of maltose, gives rise to a series of products intermediate between it and the β-glucosidomaltose.

We apply the term maltodextrin to all those non-crystalline, intermediate products of the action of diastase on starch possessing cupric-reducing power, with the exception of β-glucosidomaltose and *iso*maltose, which we regard as sugars, because they yield well-defined phenylosazones. The well-known fact that when potato starch or a solution of soluble starch is hydrolysed with malt diastase, maltose and a series of maltodextrins are produced, seems at first to stand in conflict with the results previously described on the hydrolysis of amylopectin or αβ-hexa-amylose. We have observed, in the course of an extended study of the kinetics of the different products of hydrolysis of starch, that amylopectin and its derivatives, αβ-hexa-amylose, and the maltodextrins (including the stable dextrin) exhibit marked differences when they are submitted to hydrolysis with malt diastase in presence or in absence of maltose. Further, a variety of factors such as mass of diastase relative to

that of the substances undergoing change, temperature, etc., are of influence in determining the nature of the products.

It is a general rule in reactions brought about in presence of enzymes that, as the products of change accumulate, the velocity of the reaction slackens. In many cases the phenomenon is so marked that the reaction in its final stages no longer obeys an ordinary single law of mass action. The several hypotheses adduced in explanation of this phenomenon may be summarised as follows: First, it may be due to the reduction of concentration of the substrate; secondly, it may arise from the retarding action of the products of the reaction as they accumulate; and thirdly, in the case of a substrate such as starch paste, it is conceivable that one constituent is hydrolysed more rapidly than the others according to the conditions of the experiment. The second and third hypotheses taken together furnish, in the light of our experiments, an explanation of the difference in the products formed from starch as a whole and from amylopectin, respectively, when these are submitted to the action of malt diastase.

Wohl and Glimm (*Biochem. Z.*, 1910, **27**, 349) have shown that the presence of maltose retards the complete hydrolysis of starch. We find that when a mixture of 1 part of αβ-hexa-amylose and 2 parts of maltose—the proportions obtained from starch by the action of diastase from ungerminated barley at 50°—is submitted to the action of malt diastase at 55°, the reaction soon slackens, just as it does in the case of starch paste or of soluble starch solution. At this point the percentage of apparent maltose * deduced from the cupric-reducing power amounts to 78—80% of the total dissolved solids, and the specific rotatory power is $[\alpha]_D$ 146·5—147°. Moreover, these values remain constant when the incubation period is extended to 3 hours. The constants are substantially those of equation 8 of Brown and Heron (J., 1879, **35**, 647) and it will be remembered that Brown and Morris (J., 1885, **47**, 543) and Brown and Millar (J., 1899, **75**, 315) separated from starch degraded to this stage a substance which they designated "stable dextrin." This substance, of the existence of which as an actual chemical entity there is some doubt, we regard as a maltodextrin of the highest type.

The early history of the maltodextrins is well known (see Herzfield, *Bied. Zentr.*, 1880, 347; Brown and Morris, *loc. cit.*; Brown and Millar, *loc. cit.*). The last-named give the constants of maltodextrins as $[\alpha]_D$ 181—183° and *R* 42—43. Maltodextrin is a non-crystalline

* The percentage of apparent maltose produced depends to some extent on the diastatic power of the enzyme employed. In the case of malts or of diastase preparations which are very active the percentage of apparent maltose may be much higher (see Ling, *J. Inst. Brewing*, 1922, **28**, 838).

substance and according to Brown and his colleague it is unfermentable by *Saccharomyces cerevisiæ*, and completely converted into maltose by malt diastase. Two members of the maltodextrin series were isolated and examined by Ling and Baker (J., 1895, **67**, 703; 1897, **71**, 517). They describe them as maltodextrin-α and -β, respectively. The α-substance has the formula $C_{36}H_{62}O_{31}$ and the constants $[\alpha]_D$ 180° and *R* 32·8, whilst the β-substance has the formula $C_{24}H_{42}O_{21}$ and the constants $[\alpha]_D$ 171·6° and *R* 43.

We may state that as a result of a thorough examination of the products of hydrolysis of starch under diverse conditions, we are led to conclude that only three distinct types of maltodextrin exist, namely, stable dextrin, maltodextrin-α, and maltodextrin-β. Making use of the constants published by Ling and Baker, it is possible to assign to the substances their position in the series and their respective constitutions. On the other hand, we felt that the properties of the stable dextrin and its method of isolation as previously described needed some revision.

We find that when αβ-hexa-amylose is hydrolysed with malt diastase in absence of maltose it yields one part of maltose and two parts of *iso*maltose, whilst in presence of maltose it yields a mixture of maltose and *iso*maltose, the relative quantities of which are governed by several factors such as temperature, quantity of diastase, etc., but the limit in this case is two parts of maltose and one part of *iso*maltose. Further, it seems that when amylopectin is hydrolysed by malt diastase in presence of maltose, one-third appears as maltose, whilst the remainder appears as the stable dextrin, an apparent resting stage having been reached exactly as described by Brown and Morris (*loc. cit.*). The question arises, however—Is the stable dextrin formed when amylopectin or αβ-hexa-amylose is hydrolysed in absence of maltose? This question was answered by studying the hydrolysis of αβ-hexa-amylose and of the stable dextrin in absence of maltose.

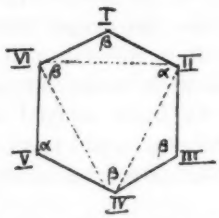
If the velocities of hydrolysis were identical in both cases, the answer would be in the affirmative. We find, however, that αβ-hexa-amylose is hydrolysed nearly three times as rapidly in absence of maltose as it is in presence of maltose or when the stable dextrin itself is hydrolysed under identical conditions. Since we have satisfied ourselves that this difference cannot be attributed to any conceivable disturbing factor, we can only conclude that the stable dextrin is not produced when αβ-hexa-amylose is hydrolysed with malt diastase under the conditions described in absence of maltose.

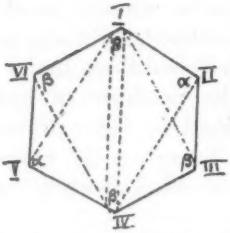
When starch paste is treated with malt diastase, two distinct phenomena occur, *viz.*, saccharification and "liquefaction." The

optimum temperature of the former is 55°, and that of the latter about 70°. The term "liquefaction" is an expression of the fact that when starch paste is treated with malt diastase it loses its viscosity and is transformed into a limpid solution of so-called soluble starch,* a change we now know to be due to the dephosphating of the amylopectin. Since, therefore, the two phenomena, saccharification and liquefaction, are quite distinct, there was no reason to suppose that their temperature optima were the same. Our results show that the optimum temperature of hydrolysis of αβ-hexa-amylose by malt diastase, like that of α-hexa-amylose, is near 50°.

It has long been known that when a solution of malt diastase or an extract of malt is heated above 65°, a distinct change is brought about in the enzyme, restricting its chemical activity. No satisfactory explanation of this phenomenon has heretofore been adduced. The mechanism of the transformation of αβ-hexa-amylose at 50° and 70° respectively is explained by the following skeletal formulæ for this amylose, in which the dotted lines show the direction in which the fission takes place.

At 50°.





At 70°.

We find that at 50° malt diastase causes a fission between the linkings at II, IV, and VI, giving rise to three dihexose molecules as above mentioned. At 70°, on the other hand, the enzyme acquires the property of breaking the chain at linkings I and IV, giving rise to two trihexose molecules which are capable of undergoing further fission at linkings I—III, I—V, II—IV, and IV—VI, giving rise to two dihexose molecules and two hexose molecules.

The production of glucose by the hydrolysis of starch with malt diastase at 70°, first pointed out by Ling and Baker (J., 1895, **67**, 702, 739) and confirmed by Ling and Davis (*J. Fed. Inst. Brewing*, 1902, **8**, 475; J., 1904, **85**, 16), has been misunderstood by many chemists as being due to the action of the enzyme maltase, which, we may point out, is no longer active above 55°. The total quantity

* Soluble starch prepared in this way shows slight cupric-reducing power even if prepared at so high a temperature as 75°, for at that temperature malt diastase still shows some very slight saccharifying power towards amylose. Both saccharifying and liquefying power are destroyed at 80°

of glucose produced under these conditions is 10—11% of the starch. It is shown to be derived exclusively from the hydrolysis of β-glucosidomaltose.

The existence of the stable dextrin was first recognised by Brown and Morris in 1885 (*loc. cit.*) as an invariable product of the hydrolysis of starch paste by malt diastase at 50°, and the determination of its nature and constitution is a problem of the highest importance alike from the academic and practical points of view. To the chemist, the existence of the stable dextrin has presented a barrier which seemed unsurmountable in arriving at any definite conclusions regarding the constitution of starch, whilst to the industrialist it has a special economic importance.

Although it has not been found possible to arrive at definite conclusions regarding the constitution of the stable dextrin from the work of earlier investigators when viewed from the present state of our knowledge, most of it has proved invaluable to us. Indeed, progress would have been impossible without the technique laid down by such workers as Horace T. Brown in a field of chemistry such as that of the polysaccharides, which abounds with pitfalls.

The course we adopted in attacking the problem of the constitution of the stable dextrin was to study first the origin of the dextrin, secondly the conditions under which it is formed, and lastly the nature of its products of hydrolysis with malt diastase. After having worked in these directions, we have arrived at definite conclusions regarding the nature of the compound from a study of its products of hydrolysis with malt diastase under various conditions.

In their work on the stable dextrin, Brown and Millar (J., 1899, **76**, 315) appear not to have paid sufficient attention to its isolation in quantitative yield and in a state in which as little alteration as possible had taken place, a matter of fundamental importance if any conclusions regarding the nature and constitution of the substance are to be drawn from experimental work with it. Our first efforts, therefore, were to discover a method by which the dextrin could be isolated quantitatively in the same condition as it is present in a starch conversion carried down to the apparent resting stage. We had therefore constantly to keep in mind the point that at no stage in its isolation and purification must any change be brought about in the dextrin molecule. Brown and Millar (*loc. cit.*) employed an elaborate method of purifying their product, and, from considerations which we will now put forward, we believe the treatment to which they subjected it must have given rise to modifications in its character.

We have already stated that in the production of the stable

dextrin one-third of the αβ-hexa-amylose (11·1% on the starch) is hydrolysed with the production of maltose, which together with the 66·6% of α-hexa-amylose (converted entirely into maltose) gives a total of 77·7% of the starch converted into maltose in a conversion brought to the stable dextrin stage, the remaining 22·3% appearing as stable dextrin. We have found that when potato starch is hydrolysed at about 40° with precipitated malt diastase from ordinary brewery malt having a diastatic power on the Lintner scale of about 30°, until the percentage of apparent amylose (estimated as maltose), expressed on the original dry starch, reaches 80·8°, the specific rotatory power is invariably $[\alpha]_D$ 147—148°. When such a conversion liquid is fermented with yeast, 77·5—78·0% of the original reducing power disappears and the residue shows $[\alpha]_D$ 185° and R 14. The yield of this unfermentable residue calculated on the anhydrous starch is uniformly 22%. Here, then, we have effected a quantitative fractionation of a starch conversion brought to the stable dextrin stage into two portions in the proportion of 78% of the former and 22% of the latter, which we regard as the stable dextrin. We shall now show that the rotatory and the reducing power of these fractions account exactly for the constants of the mixture within the limits of experimental error. Thus $[\alpha]_D$ $-1/100$ $(78 \times 138 + 22 \times 185) = X = 148{\cdot}3$, where X is the specific rotatory power of the resulting mixture. Again, $R - 1/100$ $(78 \times 100 + 22 \times 14) = Y = 81{\cdot}0$, where Y is the reducing power of the mixture.

If, now, we examine the constants recorded by Brown and Millar, expressed on the same basis, we shall find that they do not account for the optical and reducing values of the stable dextrin mixture as determined by us. Thus :

$$[\alpha]_D \; 1/100 \; (77{\cdot}8 \times 138 + 22{\cdot}2 \times 195{\cdot}5) = X = 150{\cdot}7°,$$

and $$R \; 1/100 \; (77{\cdot}8 \times 100 + 22{\cdot}2 \times 6) = Y = 79{\cdot}1.$$

From these values it will be seen that the calculated value of the specific rotatory power of the mixed products is higher, whilst that of the reducing power is lower, than the same constants calculated from our values.

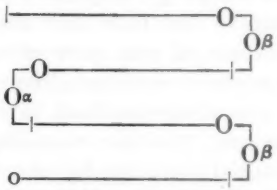
It will be shown that when the stable dextrin is hydrolysed in presence and in absence of maltose, there is no appreciable difference in the velocity of the reaction, which only becomes perceptible in the later stages after the reaction has proceeded for a protracted period.

The velocity of hydrolysis of the stable dextrin increases in the range 30—40° with a maximum at 40° and then decreases. In the initial stages the optimum temperature varies according to the period of hydrolysis.

When a solution of the stable dextrin is hydrolysed for a protracted period at 30—40°, the conversion liquid has the constants $[\alpha]_D 140{\cdot}5°$ and R 112·0, indicating distinctly the presence of glucose. When such a conversion is subjected to fermentation with yeast, 90% of the total solids are fermented away. If, now, the conversion liquid is treated with phenylhydrazine acetate, it gives only a small quantity of insoluble glucosazone but a large amount of pure maltosazone. Brown and Millar (*loc. cit.*) found that when stable dextrin was hydrolysed with malt extract it gave equal parts of maltose and glucose. We have not been able to confirm this statement with precipitated malt diastase, and therefore the production of the large amount of glucose from the stable dextrin must be attributed to the presence of maltase in the malt extract employed by Brown and Millar, which they believed was free from this enzyme (compare Ling and Nanji, *Biochem. J.*, 1923, **17**, 593). When the stable dextrin is hydrolysed with malt diastase in presence of 80% of maltose, it gives rise to a mixture of equal parts of maltose and *iso*maltose, whilst with maltase it yields *iso*maltose, and with emulsin, maltose and glucose.

There is little doubt that the basal unit of the stable dextrin is composed of four hexose residues. This will be clear from the fact that the dextrin is produced from αβ-hexa-amylose together with a third of its weight of maltose, which must necessarily entail the production of a substance containing four hexose residues. The questions now arise—What becomes of the residual valencies on the rupture of the αβ-hexa-amylose structure, and is the stable dextrin thus produced an open-chain compound or a closed-chain compound? The molecular weight of the stable dextrin is of the order of 1923, from which it may be conceived that it is an open-chain compound containing twelve hexose residues. This would account for both its reducing power and the molecular weight, but we have scarcely any practical grounds on which we can justify this view. On the other hand, it cannot be a completely closed chain structure, because it possesses a reducing power R 14. After having carefully considered both these possibilities and accounted for all the known properties of the stable dextrin, we have drawn the conclusion that it is partly composed of a closed-chain and partly of an open-chain complex, the basal molecule of both of which is the same. It is thus in fact not a single substance but a mixture, possibly a co-ordinated mixture of these two components. The next thing we have to decide is the constitution of the open-chain constituent, which primarily involves the determination of the reducing group. Is it the maltose end of the C_{24}-unit that contains the carbonyl group, or the *iso*maltose end? It will be

seen that in all the three possible structures put forward for the constitution of αβ-hexa-amylose (p. 644) the C_{24} residues on I and II have the maltose residue in the reducing end of the chain, whilst in III the reducing group is in the *iso*maltose residue as follows :

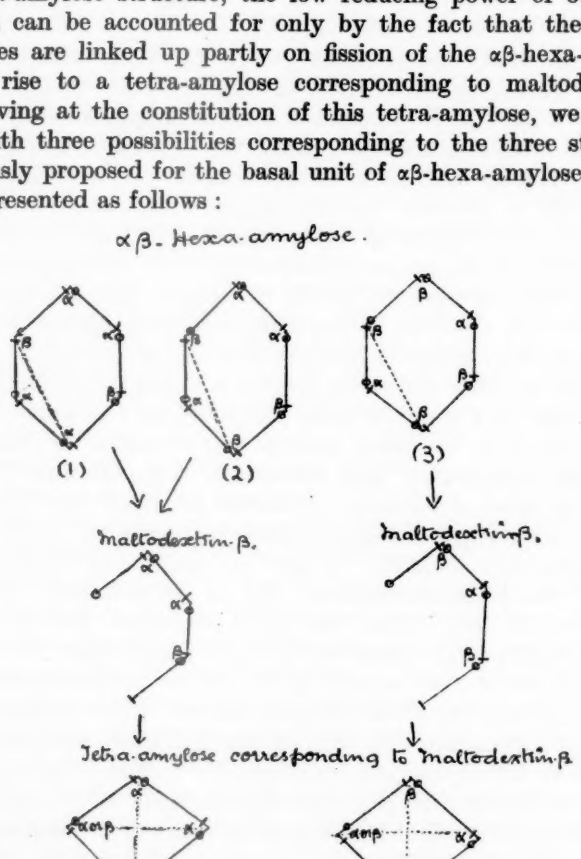


When we study the reducing power, *R*, of the different derivatives of starch, especially those of high molecular weight, we find that the value of *R* diminishes almost proportionately as the molecular weight increases, whilst the specific rotatory power increases directly with the molecular weight. We are thus brought to recognise a relation between the rotatory and the reducing powers of the products of hydrolysis of starch first assumed by C. O'Sullivan in his papers published between 1876 and 1882, and later strongly insisted on by H. T. Brown and his co-workers. The difference, however, between the way in which we adopt this rule and that in which it was put forward by the earlier workers lies in the fact that the latter interpreted their results in terms of maltose only as a standard reducing substance and a non-reducing dextrin, whereas we have proved the existence of substances, *e.g.*, β-glucosidomaltose and *iso*maltose, the constants of which differ from those of maltose. It should be added that Brown and Millar in their paper recognised that their so-called stable dextrin was a reducing substance. To give an example of the application of this rule, β-glucosidomaltose has *R* 66 compared with that of maltose, *R* 100. Thus, the above structure, having the *iso*-maltose residue as the reducing terminal group, might be expected to have *R* 40—42, if we take *R* 80—84 as the standard for *iso*-maltose. When the stable dextrin isolated by us is submitted to repeated fractionation with 86% alcohol, a fraction soluble in alcohol is obtained having the constants $[\alpha]_D$ 174·6° and *R* 38·7. A 4·1% solution of this fraction gave a mean depression 0·110°; $M = 693$.

This molecular weight is identical with that of the maltodextrin-β of Ling and Baker (*loc. cit.*), $C_{24}H_{42}O_{21}$, having the constants $[\alpha]_D$ 173·5° and *R* 43, which are substantially the same as those of the substance extracted by alcohol. We are, in fact, led to the conclusion that the stable dextrin as isolated by us is a mixture of two components, one of which is an open-chain compound identical with the maltodextrin-β of Ling and Baker, and the other a closed-

chain substance of a very much higher molecular weight and having the same C_{24}-unit representing its closed-chain basal structure.

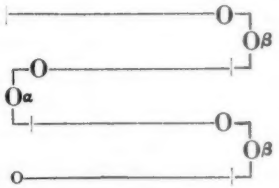
The relative proportions of these two components can be readily arrived at from the reducing power of the stable dextrin mixture, *R* 14, and that of its reducing component which has *R* 43. This would distinctly point to the fact that the two components are present in the proportion of one part of maltodextrin-β to two parts of the tetra-amylose corresponding to this maltodextrin. With regard to the fate of the residual valencies on fission of the αβ-hexa-amylose structure, the low reducing power of our stable dextrin can be accounted for only by the fact that the residual valencies are linked up partly on fission of the αβ-hexa-amylose, giving rise to a tetra-amylose corresponding to maltodextrin-β. In arriving at the constitution of this tetra-amylose, we have to deal with three possibilities corresponding to the three structures previously proposed for the basal unit of αβ-hexa-amylose. These are represented as follows:



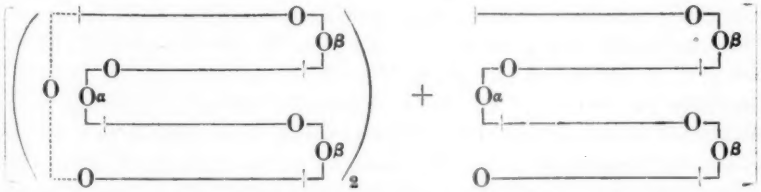
The maltodextrin derived from (1) and (2) is, it will be seen, one and the same substance, which differs from that derived from

(3) in that it has a maltose group in the carbonyl end of the molecule whilst the latter has an *iso*maltose grouping in the carbonyl end. Further, a maltodextrin of the type derived from either (1) or (2) should have at least R 50 compared with that of maltose, R 100, whilst the maltodextrin isolated by us possessed only R 38·8. The maltodextrin derived from (1) or (2) is also incapable of giving rise to maltose and glucose, as we have observed on hydrolysis with emulsin. With maltase it would give rise to considerable amounts of glucose, which also has not been observed. The maltodextrin derived from (3), on the other hand, would be expected to have R 40—42 compared with that of *iso*maltose, R 80—84. With maltase it would give *iso*maltose and with emulsin it would be hydrolysed to a mixture of maltose and glucose. All these requirements are in agreement with the conclusions already set forth for our maltodextrin, which can therefore only be derived from αβ-hexa-amylose having the structure (3).

Maltodextrin-β, $C_{24}H_{42}O_{21}$, described by Ling and Baker (*loc. cit.*), having $[\alpha]_D$ 173·5° and R 43, would therefore have the following constitution :

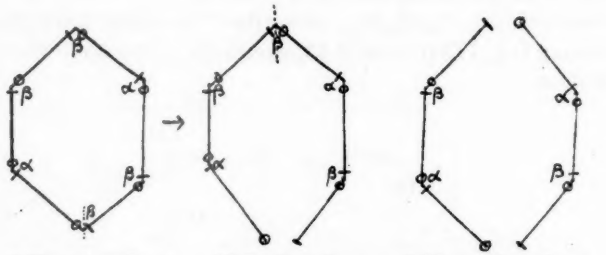


Our stable dextrin, therefore, may be represented by the following skeletal formula composed of 2 mols. of polymerised tetra-amylose corresponding to maltodextrin and 1 mol. of maltodextrin :



Maltodextrin-α described by Ling and Baker, $C_{36}H_{62}O_{31}$, has the constants $[\alpha]_D$ 180° and R 33·0. It will be seen that the value of R here again is nearly one-third of that of maltose, which further substantiates its molecular weight and also its formula. It is thus composed of six hexose residues, having a maltose residue in the carbonyl end of the compound. If there were an *iso*maltose unit in the carbonyl end of the chain, the value of R that would be required would be 27—28. It will be remembered that malto-

dextrin-α is formed when starch is hydrolysed with malt diastase at 70°. This renders the assigning of its constitution a comparatively easy task, because there is only one possibility for the fission of the αβ-hexa-amylose structure. We have seen that at this temperature fission takes place between two diametrically opposite linkings, with the formation of β-glucosidomaltose. Maltodextrin-α must therefore be regarded as an intermediate product in this degradation of αβ-hexa-amylose to β-glucosidomaltose, in the formation of which the fission of only one linking is concerned instead of the two as in the formation of β-glucosidomaltose. This, therefore, shows that in the formation of maltodextrin-α the αβ-hexa-amylose ring is simply opened up with the formation of a straight-chain compound containing six hexose residues. The constitution of maltodextrin-α and its relation to αβ-hexa-amylose and to β-glucosidomaltose will be clear from the following representation:



αβ-Hexa-amylose. Maltodextrin-α. β-Glucosidomaltose.

EXPERIMENTAL.

Hydrolysis of αβ-Hexa-amylose in Presence and Absence of Maltose.—For the purpose of these experiments two solutions were prepared. One contained 1·72 g. of αβ-hexa-amylose in 100 c.c. and the other 4·5 g. of a mixture of two parts of maltose and one part of αβ-hexa-amylose in 100 c.c. Of these solutions, 10 c.c. portions were measured into a series of test-tubes, which were placed in a metal stand and immersed in a water-bath at 55° so that the level of the water was just above the surface of the solution. A solution of precipitated malt diastase containing 1 mg. of the enzyme per c.c. was raised to 55°, and 2 c.c. of it were added to each of the test-tubes containing 10 c.c. of the solutions at the same temperature. One tube from each of the two series was withdrawn at different intervals, and the contents were washed into a 100 c.c. flask containing a drop of 10% caustic soda solution. The solutions were then made up to 100 c.c. and titrated against Fehling's solution. A 100 c.c. portion of the 4·5% solution containing a mixture of

2 parts of maltose and 1 part of αβ-hexa-amylose was converted side by side of the test-tube experiments with 20 c.c. of diastase solution at 55° for the purpose of determining the final constants. The results are shown in the following table :

Rate of Hydrolysis of αβ-Hexa-amylose in Presence and in Absence of Maltose.

Time in hours.	Percentage of apparent maltose produced.		Percentage of apparent maltose produced from hexa-amylose.	
	Hexa-amylose and maltose.	Hexa-amylose alone.	In presence of maltose.	In absence of maltose.
½	70·60	63·3	17·42	63·3
1	75·04	66·8	29·78	66·8
2	—	70·6	—	70·6
3	77·97	73·0	38·12	73·0
4	79·35	73·2	42·0	73·2
5	79·70	73·0	42·98	73·0
6	79·70	73·4	42·98	73·4

The specific rotatory power of the solids in the solution containing αβ-hexa-amylose and maltose after being incubated at 55° for 6 hours was $[\alpha]_D$ 146·5—147°, whilst, when the incubation period was prolonged for a week, it was $[\alpha]_D$ 138·2°, the reducing power being *R* 98·1. When the last-mentioned conversion liquid was inoculated with *Sac. cerevisiæ*, 89% of the reducing power, expressed as maltose, had disappeared after fermentation was complete, thus indicating the presence in the fermented liquid of some 11% of *iso*maltose (expressed on the original solids in the mixture), which sugar was identified by its phenylosazone.

When a solution of αβ-hexa-amylose alone was incubated at 55° for a week with malt diastase, the constants of the dissolved solids were $[\alpha]_D$ 141·0° and *R* 91·0. After fermentation, about one-third of the total solids in the solution had disappeared and the remaining portion had a reducing power of *R* 79·4. The dissolved solids were shown to consist of *iso*maltose, which was identified by the osazone.

Velocity of Hydrolysis of the Stable Dextrin and of αβ-Hexa-amylose by Malt Diastase at 55°.—To determine the velocity of hydrolysis of the stable dextrin and of αβ-hexa-amylose with malt diastase, a solution containing 1·13 g. of the stable dextrin (which was prepared in the manner to be described later) and another containing 1·7 g. of αβ-hexa-amylose were submitted to the action of malt diastase at 55° in the manner described in the previous section for αβ-hexa-amylose, the quantity of diastase used being 0·02 g. per 100 c.c. The following table gives the results :

Time in hours.	Percentage of stable dextrin hydrolysed in terms of maltose. A.	Percentage of αβ-hexa-amylose hydrolysed in terms of maltose. B.	Calculated percentage of potential stable dextrin produced from αβ-hexa-amylose hydrolysed in terms of maltose.* C.
½	—	63·3	45·0
1	—	66·8	50·2
2	—	70·6	55·9
3	21·0	73·0	59·5
4	—	73·2	59·8
5	—	73·0	59·5
6	26·2	73·4	60·1
16	40·0		
64	59·8		

* The values in column C were calculated from those in column B by the formula $100\ (B - 33{\cdot}3)/66{\cdot}6$, in which B represents the values given in the column under that letter. It has been shown that αβ-hexa-amylose yields one-third of its weight of maltose when hydrolysed in presence of maltose. The difference, $B - 33{\cdot}3$, would therefore represent the percentage of maltose derived from the remaining 66·6% of stable dextrin.

Determination of the Optimum Temperature of Hydrolysis of αβ-Hexa-amylose with Malt Diastase.—Portions of 25 c.c. of a solution containing 1·2 g. of αβ-hexa-amylose in 100 c.c. were measured out into each of a series of flasks and incubated at the undermentioned temperature in presence of 2·5 c.c. of a solution containing 1·25 mg. of precipitated malt diastase. At the end of 1½ hours the solutions were rapidly raised to the boiling point, cooled, and made up to 100 c.c. The reducing power, expressed in terms of maltose, was then determined iodometrically in 50 c.c. of the liquid by the method of Baker and Hulton (*Biochem. J.*, 1920, **14**, 754). The results are given in the following table:

Temp.	30°	40°	50°	60°	70°
Rel. quant. of maltose produced	2·7	3·0	3·4	2·9	1·8

Velocity of Hydrolysis of αβ-Hexa-amylose at 70°.—A solution (250 c.c.) containing 1·2 g. of αβ-hexa-amylose was treated with a solution of precipitated malt diastase which had been previously treated at 70° for ½ hour, and the velocity of hydrolysis was followed as usual by determining the reducing power at definite intervals. The results are shown in the table, where a is the percentage of αβ-hexa-amylose hydrolysed to β-glucosidomaltose:

Time (min.)	15	30	150	210
a.	6·7	9·3	29·7	39·9

Preparation of the Stable Dextrin.—A paste containing 7—8% of prime potato starch per 100 c.c., representing about 1 kg. of starch (containing 20% of moisture), was treated with 0·5 g. of precipitated malt diastase at 40°. We have purposely avoided the use of malt extract, which not only introduces impurities difficult to remove from the final dextrin, but also contains the enzyme

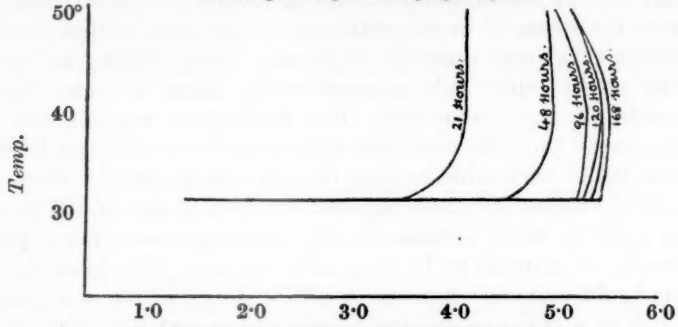
maltase, which would modify the constants of the conversion. Further, we did not consider it safe to hasten the liquefaction of the paste by raising it to the optimum temperature of liquefaction in presence of a small quantity of diastase before adding the main quantity at 40°, since this unquestionably alters to some extent the course of the conversion. The hydrolysis was allowed to continue at 40° until the constants approached $[\alpha]_D$ 148° and *R* 80·8.

It was found preferable to stop the conversion when it stood at *R* 80, since during the time required for raising the liquid to the boiling point a slight increase in the reducing power takes place and usually it is found to be *R* 81 after boiling. The filtered conversion liquid was concentrated to a thin syrup, which was poured while hot in a thin stream into a large volume of 95% alcohol so that the final strength of the alcohol in the mixture was about 85—86%. The precipitated dextrin was then kneaded for several hours with alcohol of the strength just mentioned. The crude dextrin removed from the alcoholic liquid amounted to 450 g. for every kilogram of anhydrous starch employed; it had a reducing power corresponding with 60% of maltose. It was dissolved in sufficient water to make a 15% solution, and, after boiling off the alcohol, it was sterilised and fermented with fresh brewers' yeast for about a week, when fermentation was complete. It may be remarked that fermentation of maltose proceeds slowly in presence of the colloidal dextrin. Attempts to separate the stable dextrin and maltose by dialysis proved unsuccessful, even when the dialysis was carried out against a strong current of running water.

If the fermented product had a reducing power above *R* 14, it was again fermented until this point was reached, when the solution no longer gave a crystalline phenylosazone. After decolorising with norit, the solution was dialysed to free it from mineral matters. It was then concentrated on a water-bath to a syrup, which was spread on a level glass surface placed in contact with a metallic plate at 40°. In this way a perfectly dry film was obtained in about 12 hours. The film was removed with a knife and powdered. It was thus obtained as a slightly hygroscopic, white powder having the constants $[\alpha]_D$ 185° and *R* 14. The fact already mentioned that these constants are in harmony with those of the stable dextrin–maltose mixture shows that no alteration has been brought about by the method of isolating the dextrin. The yield is almost theoretical, *i.e.*, about 22% of the dry starch employed.

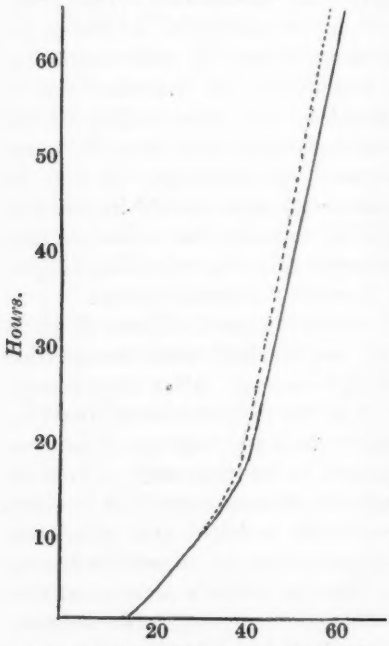
The product thus obtained was quite free from ash and nitrogen, and on submitting its aqueous solution to dialysis for a long period no change in its constants was observed. With alcohol, however, it behaved peculiarly in that on fractionation its specific rotatory power increased whilst its reducing power decreased. A 9·1%

Variations in the optimum temperature for the hydrolysis of the stable dextrin with different periods of hydrolysis.



Relative amounts of apparent maltose produced.

Rate of hydrolysis of the stable dextrin in presence and in absence of maltose.



Per cent. of stable dextrin hydrolysed expressed as apparent maltose.

····· *In presence of maltose.*

—— *In absence of maltose.*

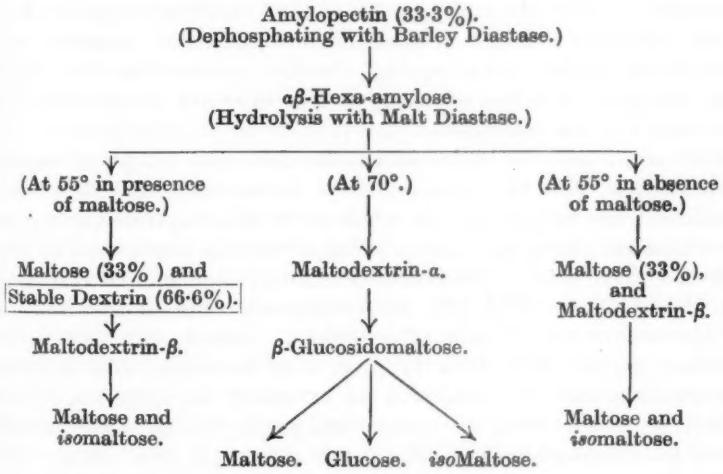
solution of the preparation gave a mean depression of 0·088°; *M* 1923, which is very much lower than that of Brown and Millar, *viz.*, *M* 6221. It must be mentioned, however, that the molecular weight of our product also increases on fractionation but not on dialysis. Our stable dextrin is acted upon slowly by maltase, giving *iso*maltose, and by emulsin, giving maltose and dextrose. Having now dealt with the properties of our stable dextrin, we shall pass on to a description of the different quantitative experiments on its transformation with diastase under different conditions.

Velocity of Hydrolysis of the Stable Dextrin in Absence of Maltose and in Presence of 78% *of Maltose.*—A 2·2% solution of the stable dextrin and a 10% solution of a starch conversion containing 22% of the stable dextrin and 78% of maltose were treated at 55° with 0·02 g. of precipitated malt diastase for every 100 c.c. of the solution, and the velocity of hydrolysis was followed in the usual manner by determining the reducing power at different intervals. The results are shown graphically in the above curves.

Velocity of Hydrolysis of the Stable Dextrin at Different Temperatures.—A 2·2% solution of the stable dextrin was treated with 0·15 g. of precipitated malt diastase for every 100 c.c. of the solution, together with a little toluene, at the different temperatures indicated in the following table, and the velocity was followed in the usual manner by determining the relative amounts of maltose produced.

Time in hours.	Relative amount of maltose produced at $T°$.		
	30°.	40°.	50°.
0	2·1	2·1	2·1
21	6·8	8·0	8·0
48	8·8	9·8	9·6
96	10·4	10·6	9·8
120	10·6	11·0	10·2
144	10·8	11·0	10·2
168	11·0	11·2	10·2

The hydrolysis of starch by barley and malt diastase is epitomised in the following scheme.



The expenses connected with these investigations have been partly defrayed by a grant from the Government Grant Committee of the Royal Society, to whom our thanks are due. We have also to express our thanks to Mr. W. J. Harper for carrying out much of the analytical work herein described.

BRITISH SCHOOL OF MALTING AND BREWING AND
DEPARTMENT OF THE BIOCHEMISTRY OF FERMENTATION.
UNIVERSITY OF BIRMINGHAM. [*Received, September 23rd,* 1924.]

XCIV.—*Studies on Starch. Part IV. The Nature of the Amylo-hemicellulose Constituent of certain Starches.*

By Arthur Robert Ling and Dinshaw Rattonji Nanji.

In Part I of these studies (J., 1923, **123**, 2671) we have confirmed the observations of Schryver and his co-workers that certain starches, notably those of barley, wheat, rice, etc., contain a substance of the nature of a hemicellulose (see Schryver and Thomas, and Clayson and Schryver, *Biochem. J.*, 1923, **17**, 493, 497).

This "amylo-hemicellulose," as we prefer to designate it, is widely distributed in nature and occurs in considerable quantities, especially associated with starch, in the different starch-bearing fruits and seeds. It also appears to be present in leaves and stems and seems to be one of the principal constituents of the cell walls of such plants, formed at a very early stage of their development. In the different woods we have examined, it is also present in varying quantities. Since the main portion of the hemicellulose gives a blue iodine reaction, it might be confused in some cases, notably when present in woods, with starch. Another polysaccharide, which does not give an iodine reaction, present in starch to the extent of less than 1% was contained in the product isolated by us.

Our view, that the silica in the hemicellulose exists in organic combination with the polysaccharide as an ester, has now been confirmed, and we find that the whole of the silica is present in organic combination, the hemicellulose being a calcium-magnesium or iron salt of a silicic ester. The recent work of Pringsheim and Kusenack (*Z. physiol. Chem.*, 1924, **137**, 265) on lichenin is but another instance of the occurrence of such silicic esters. Indeed, our view is fast gaining ground that silica fulfils a very important *rôle* in plant metabolism, and the results of an extended investigation in this direction, mainly from an agricultural point of view, have already been published elsewhere (Nanji and Shaw, *J. Soc. Chem. Ind.*, 1925, **44**, 1T).

This hemicellulose is not acted on by the diastase of ungerminated barley even after prolonged incubation at 50°, whilst the other two constituents of the starches are hydrolysed or rendered soluble by this enzyme. We have thus a ready means of isolating the hemicellulose. It is hydrolysed by diastase of germinated barley (malt) and we have now ascertained the products of hydrolysis at different temperatures and the velocity of the reaction when this enzyme is employed.

Preliminary experiments showed that whilst there is no essential difference between precipitated malt diastase and a freshly-prepared

extract of malt, the latter is very much quicker in its action and brings about the hydrolysis more completely than precipitated malt diastase, which is uncertain in its action in the final stages, and leaves 15—16% of the hemicellulose unhydrolysed. When a concentrated paste of the hemicellulose is hydrolysed with malt extract, and the liquid tested from time to time with iodine, it is found that the iodine coloration disappears rapidly and is not given either by the residuum or by the clear conversion liquid, but if the former be boiled with a little water, it again gives a strong blue colour with iodine.

Experimental.

Preparation of the Amylo-hemicellulose.—A 10% paste of wheat or rice starch (1 kilo.) is hydrolysed at 50° with a cold water extract of barley corresponding to about 200 g. of finely-ground barley. The mixture is kept at 50° for 12—24 hours, when the hemicellulose usually flocculates. The liquid is centrifuged and the flocculum of the hemicellulose is repeatedly washed on the centrifuge until the washings are free from reducing sugars. The flocculum is boiled with water and again submitted to the action of barley diastase and washed free of reducing sugars. Another method we adopted for freeing the hemicellulose from reducing sugars, which involved less trouble, consisted in transferring the flocculum to muslin bags, which were immersed in a current of running water. The process of osmosis was carried out in presence of a piece of camphor and was considerably expedited by alternatively raising and lowering the bags in the water. The flocculum, after being thus freed from the reducing sugars, was dehydrated with 90% alcohol and then with absolute alcohol, when it was obtained as an amorphous, white powder practically insoluble in cold water. The yield of the product was about 7—8% from wheat starch and 15% from rice, which are below the amount actually found by analysis, as will be shown later. The loss incurred, principally during washing, is only of the order of about 3%. The product is quite free from pentose, and on hydrolysis with mineral acids silica separates out from the hydrolysed liquid; and this is the reason why pastes of starches, such as barley, wheat, rice, etc., which contain this hemicellulose, always remain turbid, even on complete hydrolysis. In hot water it gives a gelatinous paste which with higher concentration almost sets to a gel on cooling. The hemicellulose thus obtained is quite free from nitrogen, although it is never free from ash. The ash of several preparations was uniformly 1·2—1·3%, which consisted principally of silica, phosphoric acid, calcium, magnesium, and iron. The amounts of calcium, magnesium, and phosphoric acid varied considerably, although the

percentage of silica, which constituted the major portion of the ash, was remarkably constant between 0·83—0·92% (SiO_2).

Hydrolysis of Amylo-hemicellulose with Malt Diastase.—When a paste of the hemicellulose is submitted to the action of malt diastase, it is hydrolysed rapidly, giving exclusively maltose as the final product of its hydrolysis, the velocity of the reaction being dependent on certain factors. Thus a part of the hemicellulose always remains in solid suspension in the colloidal solution of the remainder, and the latter portion is rapidly hydrolysed, whilst the portion in suspension is unaffected. This introduces difficulties in the studies on the kinetics of its hydrolysis with malt diastase under different conditions. It would have been possible to overcome this difficulty and get a homogeneous substrate by heating it in an autoclave which had a liquefying action, but as we intended to get a true picture of the behaviour of the hemicellulose, exactly as it exists in nature, with diastase, we surmounted this difficulty by employing a dilute solution and so arranging the amounts of enzyme and the substrate (in colloidal solution) that the latter was not completely hydrolysed.

Optimum Temperature for the Hydrolysis of the Hemicellulose with Malt Extract.—Several 0·25 g. portions of the hemicellulose were each transferred carefully to 100 c.c. flasks and thoroughly gelatinised with 50 c.c. of water, and after bringing their contents to the temperatures indicated below, they were treated with 2·5 c.c. of a cold water extract (1 part of malt to 2·5 parts of water) of low-dried malt, the latter being brought to the respective temperatures before addition to the hemicellulose solution. A blank solution containing the equivalent quantity of malt extract in 50 c.c. of the solution was also kept side by side with each experiment. The hydrolysis was stopped at the end of 1 hour by rapidly bringing the solutions to the boiling point. The solutions, after cooling, were made up to 100 c.c. and filtered, and the reducing power of 50 c.c. of the filtrate was determined iodometrically. The relative amounts of maltose produced after correcting for the reducing power of the malt extract used are as follows, from which it will be seen that the optimum is about 50—55°, whilst there is practically no hydrolysis of the hemicellulose taking place at 70°.

Temperature	30°	40°	50°	55°	60°	70°
Rel. amounts of maltose produced	6·0	6·5	7·0	7·0	6·0	0·0

Rate of Hydrolysis of Hemicellulose at Different Temperatures.—A 1·6% paste of the hemicellulose was treated at the different temperatures with 5·0 c.c. of a cold water extract of malt (prepared as before) for every 100 c.c. of the paste. 50 c.c.-Portions were withdrawn at different intervals and the action was stopped by

boiling. The portions were cooled, made up to 100 c.c., filtered, and the rate of hydrolysis followed as usual by determining the reducing power after correcting for that of the malt extract used. The results are given in the following table, where t is the time in minutes and m the relative amounts of maltose produced :—

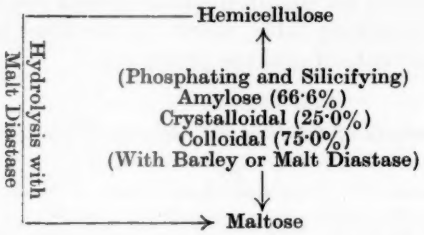
Velocity of Hydrolysis of the Hemicellulose at Different Temperatures.

30°.		50°.		70°.	
t.	*m.*	*t.*	*m.*	*t.*	*m.*
15	10·4	15	18·5	15	3·5
30	15·6	45	19·5	30	3·6
105	19·7	60	20·0	45	3·7
165	20·6	120	20·0	60	3·9
285	23·2	300	20·8	120	4·2
345	23·3	360	22·6	300	5·0
		450	23·1		

When a paste of hemicellulose was treated for a protracted period with a solution of precipitated malt diastase at 50°, and the liquid filtered from the insoluble residuum, the solids in the filtrate approximated to about 84—85% of the original hemicellulose taken, and had the constants $[\alpha]_D$— 137·4° and R 98·3. If a little of the conversion liquid was treated with *Saccharomyces cerevisiæ*, the sugar was completely fermented away, as observed by the complete disappearance of reducing power. With phenylhydrazine acetate it gave maltosazone, m. p. 193°, which, when examined microscopically, was quite free from crystals of the *iso*maltosazone type. The residue from the above conversion gave a bluish-purple coloration with iodine. It was boiled again with water and, on reconverting with precipitated malt diastase, gave exclusively maltose. This was further confirmed by hydrolysing hemicellulose with a freshly prepared malt extract (which hydrolyses hemicellulose more rapidly) and examining the fermentability of the sugar in the conversion liquid, which was also completely fermented away. There is no doubt, therefore, that the sugar produced by the complete hydrolysis of hemicellulose is exclusively maltose. This fact distinctly shows that it is a derivative of α-hexa-amylose, and this would be further substantiated by the characteristic similarity in the behaviour of both α-hexa-amylose and the hemicellulose with malt diastase at 70°. The differences in the physical properties of these two substances would be, in all probability, due to the esterification of the α-hexa-amylose with silicic acid, and we hope to gain further information on this point by attempting to prepare synthetically the silicic esters of the carbohydrates.

The relationship between hemicellulose and polymerised α-hexa-

amylose and their hydrolysis with diastase are epitomised in the following scheme.



Determination of Amylo-hemicellulose in Starches.—The hemicellulose content of starches has been found to vary within wide limits and to depend to a very large extent on the state of division of the amylaceous material and the degree of fractionation to which it has been submitted during manufacture. It can be readily estimated as follows: A known weight of the starch is gelatinised thoroughly by boiling and treated at 50° with barley diastase corresponding to about 10 g. of barley for 2·5 g. of the dry starch. The conversion liquid is made up to 200 c.c. together with the hemicellulose flocculum and filtered. The density of the filtrate is taken and from the excess density the percentage of the total solids is determined by dividing it by the factor 3·95. Two-thirds of the solid matter in the conversion liquid being maltose, and the rest αβ-hexa-amylose, the former is expressed as anhydrous starch by multiplying by the factor 0·9473. The weight of total solids, after correction for the water of hydration of maltose, is subtracted from the weight of the anhydrous starch taken, and the difference gives the hemicellulose. Rice starch contains 19·15%, wheat 10·0%, and barley 7·68%, but these values vary according to the process of manufacture adopted.

Our thanks are due to Sir Richard Garton for supplying us with samples of starches, and to Professor C. J. Lewis for allowing us the use of his electric centrifuge. Further, we have to acknowledge the assistance of Mr. W. J. Harper, who has carried out many of the analyses herein recorded. A portion of the expenses connected with this work has been defrayed by a grant from the Government Grant Committee of the Royal Society, to whom also our thanks are due.

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University of Birmingham. [*Received, September 25th,* 1924.]

XCV.—*The Thermal Decomposition of Nitrogen Pentoxide.*

By Herbert S. Hirst.

In recent years considerable interest has centred round the subject of the velocity and mechanism of unimolecular reactions. For the simplest type, namely, homogeneous reaction in the gaseous phase, there have been many attempts to develop a theoretical interpretation, and various expressions for the rate have been published from time to time. Very convenient summaries of the work done on this subject have been presented by Tolman (*J. Amer. Chem. Soc.*, 1921, **43**, 269) and by Harned (*J. Franklin Inst.*, 1923, **196**, 181). Special reference may also be made to the recent important communications of Christiansen (*Z. physikal. Chem.*, 1922, **103**, 91) and of Christiansen and Kramers (*ibid.*, 1923, **104**, 451). All the equations obtained are of the same nature, that is to say, the reaction velocity in all cases follows an exponential law of the type $k = s\epsilon^{-Q/R\theta}$, where k is the velocity coefficient. It is in the interpretation of the quantities s and Q that the differences arise. The fundamental questions of the nature of the primary activation which precedes chemical reaction and of the mechanism of reaction itself are still largely problematical. The difficulty of any definite decision is considerably augmented in the case of a homogeneous unimolecular reaction, owing to the almost entire lack of experimental evidence whereby the many and varied theories may be put to the test. Until the present year, the experiments of Trautz and Bhandarkar (*Z. anorg. Chem.*, 1919, **106**, 95) on the dissociation of phosphine provided the only numerical data of the reaction velocity of what was thought to be a truly homogeneous non-catalytic, unimolecular reaction in the gaseous phase. Recently, however, it has been shown by Hinshelwood and Topley (J., 1924, **125**, 393) that the reaction is by no means homogeneous, the wall effect being very pronounced, and that, consequently, no valid test can be applied by the use of these results. As regards the decomposition of nitrogen pentoxide, first investigated and shown to be unimolecular in nature by Daniels and Johnston (*J. Amer. Chem. Soc.*, 1921, **43**, 53), this was supposedly ruled out, although quite homogeneous, by the discovery of an autocatalytic effect (Daniels, Wulf, and Karrer, *ibid.*, 1922, **44**, 2402). Up to the present, then, there seems to be absolutely no evidence that a true unimolecular reaction in the gaseous phase does ever occur, and in view of this Hinshelwood and Topley (*loc. cit.*) have pointed out that an investigation of the reason for such a non-existence may be

of greater importance than a continual accumulation of unverifiable theory.

It is one of the purposes of the present paper, however, to show that it is by no means improbable that the dissociation of nitrogen pentoxide may yet prove to be an example of a reaction which fulfils all the requirements of a true gaseous unimolecular decomposition. An investigation by the author of the chief evidence on which the assumed autocatalytic nature of the process depends has failed to substantiate this evidence and indeed the present results seem to point in entirely the opposite direction.

Sir J. J. Thomson (*Phil. Mag.*, 1924, [vi], **47**, 337) recently advanced an expression for the velocity coefficient of a unimolecular reaction, namely,

$$k = \frac{Q}{R\theta} \cdot \frac{U_m}{\lambda} \cdot \epsilon^{-\frac{Q}{R\theta}},$$

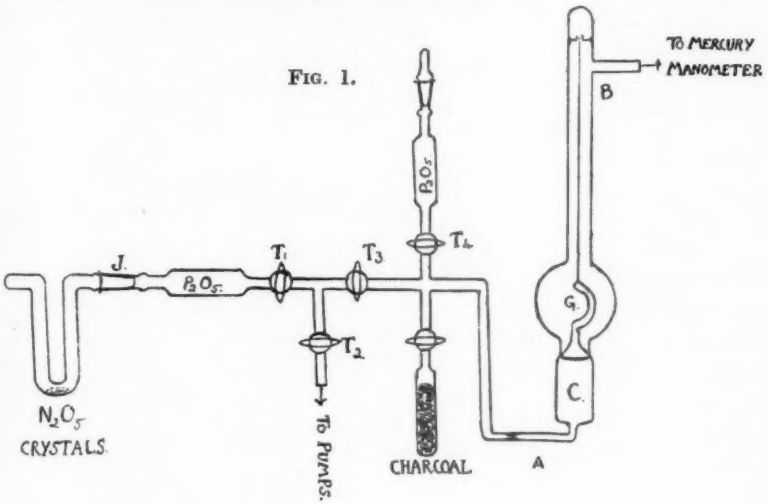
based on the view that the immediate cause of chemical reaction is the interchange of energy due to molecular impact. If such is the case, it was argued that the introduction of an inert gas, for example argon, to the reaction chamber might be expected to exercise some influence on the velocity of decomposition. The present work was originally undertaken with this in view, and the decomposition of nitrogen pentoxide was chosen as the reaction to be studied, first, on account of its homogeneity and, secondly, on account of the convenience arising from the lowness of the temperatures which may be employed. A reinvestigation of the velocity and mechanism of the dissociation was first undertaken and the present paper embodies the main results obtained.

Preparation of the Nitrogen Pentoxide.—The substance was prepared as described by Daniels and Bright (*J. Amer. Chem. Soc.*, 1920, **42**, 1131). The method consists essentially of two processes, a distillation and a sublimation, and several modifications were made in the apparatus described in the above communication with a view to minimising the time necessary for the change over from the first to the second process. After a little practice it was found quite easy to obtain good yields of the pure white crystals of the pentoxide. These were stored in air-tight U-tubes, which, to prevent rapid decomposition of the substance, were immersed in ice and salt contained in a large Dewar vessel.

Apparatus.—The apparatus used for the actual determination of the velocity was similar in general outline to that used by Daniels and Johnston, although it differed in various details of construction. The following diagram represents the more essential features. Owing to the corrosive nature of nitrogen pentoxide, all parts of the apparatus with which it came into contact had to be entirely of

glass. As tap grease, a special preparation composed of liquid and solid paraffin was used and was found to be fairly resistant, though frequent renewals were necessary. The pressure gauge, G, used in these experiments was also constructed entirely of glass after the pattern described by Jackson (J., 1911, **99**, 1066), its action being similar to that of the well-known Bourdon type. The gauge actually used enabled a change in pressure of 0·5 mm. of mercury to be measured with considerable accuracy when a compensation method was employed, the actual readings being taken on a suitable mercury manometer.

FIG. 1.



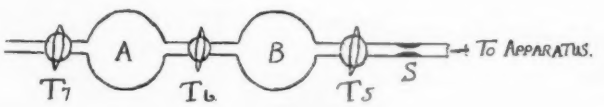
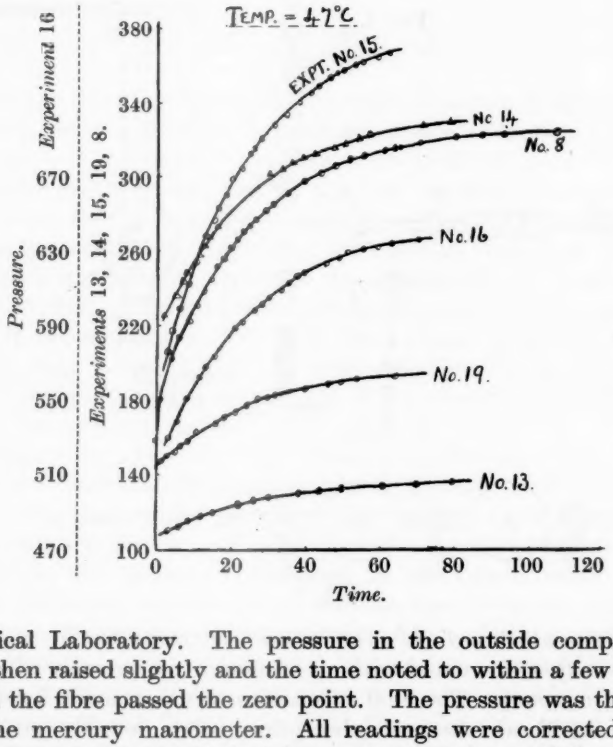


FIG. 2.

Experimental Procedure.—The whole apparatus to the right of tap T_1 was first evacuated with an oil-pump to a pressure of about 1 mm. of mercury. The final evacuation was then made by means of two liquid air–charcoal absorption tubes suitably situated. While the whole apparatus was thus evacuated, a zero reading of the glass fibre of the gauge was taken. Tap T_3 was then closed and the U-tube containing the pure pentoxide attached by the ground joint, J. The supernatant gases were pumped out two or three times to remove all traces of nitrogen tetroxide present, tap T_2 was closed, and the gaseous pentoxide allowed to pass into the reaction chamber, C, by means of taps T_1 and T_3. When approxi-

mately the desired pressure had been reached, the vessel was sealed off as rapidly as possible at A, a constriction having previously been made there to facilitate the sealing process. In cases where the effect of some foreign gas on the reaction velocity was being observed, this gas was introduced by means of tap T_4. After sealing, the vessel C was lowered into a large thermostat up to the point B. The variation in temperature of the thermostat did not exceed $\pm$ 0·01°, whilst the actual temperatures themselves were obtained from three thermometers, previously calibrated by comparison with a thermometer recently standardised at the National

FIG. 3.



Physical Laboratory. The pressure in the outside compartment was then raised slightly and the time noted to within a few seconds when the fibre passed the zero point. The pressure was then read on the mercury manometer. All readings were corrected to 0°. This process was repeated at frequent intervals, until the reaction was almost complete. The apparatus was then left for a considerable time, and a final observation taken, when the pressure became constant. Since the reaction is photosensitive, the whole experiment was carried out in a dark room. The illumination of the pointer and microscope scale was effected by a small, red lamp, which was only lit when an actual reading was taking place. Red light was

chosen on account of its photochemical non-activity, the experiments of Daniels and Johnston (*J. Amer. Chem. Soc.*, 1921, **43**, 72) having shown the active radiations to lie between the limits 460 $\mu\mu$ and 400 $\mu\mu$.

Calculation of Results.—The results were represented graphically as shown in Fig. 3, where, to save space, a selection of the curves obtained is given. The original scale used was large, 1 mm. being equivalent to 1 mm. of mercury in pressure. In the calculation of the reaction velocity coefficients, the pressure values were obtained from these curves by graphical interpolation for regular time intervals. The actual initial pressure of nitrogen pentoxide admitted was calculated in each case from the final constant pressure value. The neat, graphical methods of Daniels and Johnston (*J. Amer. Chem. Soc.*, 1921, **43**, 57) were exactly followed, but a short *résumé* of the necessary calculations is given here for easy reference. The decomposition of nitrogen pentoxide was assumed to take place according to the equation :

$$2N_2O_5 \longrightarrow 2N_2O_4 + O_2$$
$$\downarrow\uparrow$$
$$4NO_2$$

Owing to the alteration of the $N_2O_4 \rightleftharpoons 2NO_2$ equilibrium with change of partial pressure of the nitrogen tetroxide, a correction was rendered necessary. The following equations connect the various partial pressure components. When decomposition is complete, all the partial pressures being expressed in terms of that of oxygen,

$$P_f = 3P_{O_2} + 2\alpha P_{O_2},$$

where P_f is the final total pressure, P_{O_2} the partial pressure of the oxygen, and α the degree of dissociation of the nitrogen tetroxide. In the work of Daniels and Johnston, the degree of dissociation, α, was calculated from Schreber's equation, expressing the data obtained by Natanson. In the present calculations, the more recent equation given by Bodenstein (*Z. physikal. Chem.*, 1922, **100**, 78) was employed,

$$\log K = \log \frac{P_{N_2O_4}}{P^2_{NO_2}} = \frac{2891}{T} - 1{\cdot}75 \log T - 0{\cdot}0046T + 8{\cdot}92 \times 10^{-6}T^2 - 6{\cdot}8148.$$

Again, P_i, the initial pressure of nitrogen pentoxide, is obviously equal to $2P_{O_2}$.

Following the method of Daniels and Johnston, tables were constructed by giving arbitrary values to P_{O_2}, and the results embodied in large-scale graphs, whence the appropriate value of P_i could be obtained at once from the known experimental value of P_f.

Now, at any time during the reaction,

$$P = P_i + P_{O_2} + P_{N_2O_4} + P_{NO_2} - p,$$

where P is the observed pressure at time t, and p is the partial pressure that would be exerted by the pentoxide which has decomposed up to time t. Hence $P - P_i = P_{O_2}(1 + 2\alpha) = (\frac{1}{2} + \alpha)\, p$. Graphical interpolation was also employed to obtain the values of p, corresponding to experimentally determined values of $P - P_i$.

The formula for the velocity coefficient is then

$$k = \frac{2{\cdot}303}{t_2 - t_1} \log_{10} \frac{P_i - p_1}{P_i - p_2}.$$

Presentation of Results.—Table I gives the results of the calculations of the velocity coefficients from the experimental data for the decomposition of pure nitrogen pentoxide. The temperature was in all cases constant at 47°.

Experiments 2, 3, and 4 were conducted with a reaction chamber of approximate volume 25 c.c., experiment 8 in a chamber volume of 50 c.c., while in experiments 11 and 12 the vessel was packed with glass wool. The results obtained are in very good agreement among themselves, while their mean, $k = 37{\cdot}3 \times 10^{-3}$, agrees remarkably well with the calculated value, $38{\cdot}0 \times 10^{-3}$, obtained by use of the value of the critical increment deduced by Daniels and Johnston from their experiments. This was taken as 24,800 calories, and the value of k for 47° calculated by means of the equation

$$E = (1{\cdot}98 T_2 T_1 \times 2{\cdot}302 \log_{10} k_2/k_1)/T_2 - T_1,$$

where E is the critical increment and T_2 and T_1 are the absolute temperatures. The initial pressures in the above experiments were on the whole lower than those in the previous work, but it may be noted that the value of k obtained for the very low initial pressure in experiment 2, though slightly above the average, is still in good agreement. On the other hand, Daniels and Johnston found, for similar low initial pressures, values of k much above the average and Bodenstein (*Z. physikal. Chem.*, 1923, **104**, 51) has advanced a mechanism of the reaction at low pressures whereby such high values would be expected. If the correction he derives is applied to the above result, the value of k obtained is $32{\cdot}2 \times 10^{-3}$, which is now decidedly low. Indeed, this experiment by no means substantiates the theory of Bodenstein. This point, however, has not yet been further investigated.

The effect of argon on the velocity was next examined. Owing to the supposed autocatalytic nature of the reaction, the effect, if any, was not expected to be large. It seemed highly improbable, also, from a theoretical point of view, assuming reaction to be due to

TABLE I.

Experiment No. 2 (P_i = 53·5 mm.).

t.	P.	$P-P_i$.	p.	$k\times10^3$.
10	79·8	26·3	19·4	—
20	91·0	37·5	28·0	29·2
30	100·0	46·5	35·8	36·5
40	106·2	52·7	41·8	30·6
50	111·1	57·6	45·2	47·1
60	114·0	60·5	48·1	43·0
70	115·5	62·0	50·0	43·3
—	—	—	—	—
—	—	—	—	—
Inf.	120·0	—	53·5	—
			Mean	38·3

No. 3 (P_i = 121·5 mm.).

t.	P.	$P-P_i$.	p.	$k\times10^3$.
10	171·0	49·5	49·5	—
20	198·0	76·5	62·5	36·2
30	214·8	93·3	78·8	32·4
40	227·0	105·5	91·5	35·3
50	235·5	114·0	99·5	31·0
60	243·2	121·7	108·2	50·2
70	249·0	127·5	114·4	39·7
80	252·1	130·6	117·3	29·5
90	250·0	132·5	118·8	43·9
Inf.	257·5	—	121·5	—
			Mean	37·9

No. 4 (P_i = 185·0 mm.).

10	257·0	72·0	58·4	—
20	297·2	112·2	98·2	37·8
30	321·3	136·3	122·0	32·1
40	337·5	152·5	139·9	33·4
50	349·5	164·5	152·4	32·5
60	358·8	173·8	163·0	39·6
70	364·5	179·5	169·7	36·3
80	368·2	183·2	173·0	24·4
90	371·4	186·4	177·5	46·9
100	373·8	188·8	180·2	44·6
—	—	—	—	—
—	—	—	—	—
—	—	—	—	—
—	—	—	—	—
Inf.	378·5	—	185·0	—
			Mean	36·4

No. 8 (P_i = 157·6 mm.).

10	228·6	71·0	56·8	—
20	263·7	106·1	89·5	36·9
30	284·3	126·7	109·8	35·4
40	299·0	141·4	125·4	39·5
50	308·9	151·3	137·0	44·7
60	315·6	158·0	142·7	32·4
70	319·7	162·1	147·1	35·0
80	322·3	164·7	150·0	32·3
Inf.	329·2	—	157·6	—
15	247·8	90·2	73·7	—
25	274·8	117·2	100·8	39·1
35	292·3	134·7	118·0	36·0
45	304·4	146·8	130·9	39·4
55	312·3	154·7	139·4	38·3
65	318·0	160·4	145·5	40·7
			Mean	37·4

No. 11 (P_i = 186·7 mm.).

10	275·2	88·5	73·2	—
20	313·0	126·3	109·3	38·3
30	335·3	148·6	132·6	35·8
40	350·8	164·1	149·2	36·6
50	361·2	174·5	160·5	35·9
60	369·3	182·6	169·3	40·9
70	374·1	187·4	174·5	43·9
Inf.	384·8	—	186·7	—
15	295·5	108·8	92·4	—
25	325·6	138·9	122·5	38·5
35	344·0	157·3	142·0	36·2
45	356·3	169·6	155·6	36·3
55	365·7	179·0	165·7	39·2
65	372·2	185·5	172·6	39·8
			Mean	38·3

No. 12 (P_i = 195·3 mm.).

10	282·2	86·9	79·6	—
20	324·4	129·1	112·1	40·5
30	348·0	152·7	137·7	36·8
40	363·1	167·8	153·3	31·6
50	374·8	179·5	166·1	36·3
60	383·5	188·2	175·4	38·3
—	—	—	—	—
Inf.	400·8	—	195·3	—
15	305·5	110·2	93·8	—
25	337·4	142·1	126·0	38·1
35	356·0	160·7	145·6	33·2
45	369·5	174·2	160·1	34·6
55	379·7	184·4	171·2	37·9
65	386·0	190·7	178·4	35·5
			Mean	36·3

molecular impact, that any effect would be observed; for neither difference in the initial pressure of the pentoxide nor the actual gaseous products of the reaction gave rise to any measurable increase in the velocity. Both these factors would reduce the mean free path of the molecules, the volume of course remaining constant, and render collision more frequent. Since, however, as far as is known, this was the first case in which a rate of reaction had been

measured in an atmosphere of an inert gas, the experiments were carried through and the results are shown in Table II.

TABLE II.

Experiment 5 (P_i = 171·5 mm.).

Pressure of Argon admitted = 176·1 mm. Temp. = 47°.

t.	P.	$P-P_i$.	p.	$k\times10^3$.
10	243·2	71·7	58·3	—
20	279·2	107·7	93·6	37·4
30	303·4	131·9	118·0	37·6
40	318·7	147·2	134·5	36·9
50	330·0	158·5	146·4	38·8
60	337·9	166·4	155·2	43·1
70	342·7	171·2	160·8	42·1
—	—	—	—	—
Inf.	354·6	—	171·5	—
			Mean	39·3

No. 9 (P_i = 101·0 mm.).

Pressure of Argon = 108·2 mm.

t.	P.	$P-P_i$.	p.	$k\times10^3$.
10	154·4	53·4	41·1	—
20	173·5	72·5	58·0	33·2
30	188·4	87·4	71·2	36·7
40	197·6	96·6	80·0	35·0
50	203·5	102·5	85·5	30·4
60	207·8	106·8	90·3	36·1
70	210·8	109·8	93·4	35·1
Inf.	218·2	—	101·0	—
15	164·3	63·3	49·7	—
25	181·4	80·4	65·2	36·2
35	193·5	92·5	76·0	35·6
45	200·8	99·8	83·0	32·8
55	206·0	105·0	88·3	34·9
65	209·5	108·5	92·1	35·4
			Mean	34·7

No. 10 (P_i = 115·5 mm.).

Pressure of Argon = 105·5 mm.

t.	P.	$P-P_i$.	p.	$k\times10^3$.
10	179·5	64·0	50·2	—
20	201·7	86·2	70·1	36·3
30	216·5	101·0	84·3	37·5
40	226·7	111·2	95·0	42·0
50	233·8	118·3	101·8	40·3
60	238·0	122·5	106·0	36·6
70	240·2	125·7	109·0	37·9
Inf.	247·8	—	115·5	—
15	192·2	76·7	61·7	—
25	209·8	94·3	77·8	35·6
35	222·0	106·5	90·0	39·1
45	230·4	114·9	98·6	41·1
55	236·2	120·7	104·1	39·4
65	239·1	123·6	107·9	40·5
			Mean	38·7

It will be seen that the above expectations were realised, as the mean of the values of k in the three experiments, namely, $k = 37{\cdot}6 \times 10^{-3}$, is less than 1% higher than the previous value and well within the limits of experimental error. An inert gas, therefore, has no determinable effect on the velocity of this reaction, although it may be that, in this case, the catalytic effect outweighs all others.

Some doubts were entertained about the nature of this autocatalysis, one ground being that the great increase in the concentration of nitrogen tetroxide during the course of the reaction did not give the slightest indication of an acceleration of the reaction. The effects of various other gases were therefore tried with a view to obtaining further evidence of the nature and mechanism of the reaction.

The effects of a large excess of the products of reaction were first examined. Three experiments were made with excess oxygen and

two with excess nitrogen tetroxide, but to save space the data of one only in each case are given in full in the following tables.

TABLE III.

Excess oxygen present.

Experiment 14 (Temperature = 47°).

Partial pressure of oxygen admitted = 123·5 mm.

t.	P.	$P-P_t$.	p.	$k\times10^3$.
10	254·4	93·0	76·5	—
20	282·0	120·6	104·6	40·2
30	300·4	139·0	122·5	37·9
40	310·3	148·9	133·1	31·9
50	318·5	157·1	141·9	38·2
Inf.	336·5	—	161·4	—
5	235·5	74·1	59·3	—
15–	269·8	108·4	92·0	38·6
35	305·7	144·3	128·4	37·7
45	314·4	153·0	137·9	34·0
55	322·0	160·6	145·5	39·1
			Mean	37·2

Expt.	P_t.	P_{O_2} (original).	$k\times10^3$.
13	60·6	122·8	38·3
15	187·0	163·0	35·9

TABLE IV.

Excess nitrogen tetroxide present.

Experiment 16 (Temperature = 47°).

Pressure of equilibrium mixture of dioxide and tetroxide admitted = 227·5 mm. at 17·2°.

t.	P (total).	$P-P_t$.	p.	$k\times10^3$.
10	558·3	373·8	72·5	—
20	586·2	401·7	106·6	36·3
30	605·3	420·8	130·2	36·1
40	618·6	434·1	146·2	35·0
50	627·2	442·7	157·9	36·4
60	632·9	448·4	165·1	31·6
Inf.	647·5	—	184·5	—
5	536·7	352·2	47·0	—
15	573·5	389·0	91·2	38·8
25	596·4	411·9	119·2	35·7
35	612·2	427·7	139·0	36·2
45	623·4	438·9	153·1	37·1
55	630·3	445·8	161·9	33·0

Experiment 16 : Mean value $k = 35{\cdot}6 \times 10^{-3}$.
Experiment 17 : Mean value $k = 36{\cdot}7 \times 10^{-3}$.

Owing to the continuous alteration of the $N_2O_4 \rightleftharpoons 2NO_2$ equilibrium, considerable modification had to be made in the calculation of the results of experiments 16 and 17. Thus, if P_x is the pressure of the equilibrium mixture of dioxide and tetroxide introduced, from a knowledge of K, the equilibrium constant at the temperature

in question, it is possible to calculate the pressure, P_M, the gas would exert if it were all present as pure tetroxide. For

$$P_x = (1 + \alpha)P_M, \text{ while } K = P_{N_2O_4}/P^2_{NO_2} = (1 - \alpha)/(4\alpha^2 P_M)$$

and therefore $4KP^2_M - (8KP_x + 2)P_M + (4KP_x + 1)P_x = 0$ (1)

From this equation P_M can be obtained.

To calculate P_i, the new equations will be

$$P_f = P_{N_2O_4} + P_{NO_2} + P_{O_2} + P^1_{N_2O_4} + P^1_{NO_2},$$

where $P^1_{N_2O_4}$ and $P^1_{NO_2}$ are the respective partial pressures of tetroxide and dioxide in the admitted mixture.

$$\text{Hence } P_f = 2(1-\alpha)P_{O_2} + 4\alpha P_{O_2} + P_{O_2} + (1 - \alpha)P_M + 2\alpha P_M$$
$$= \tfrac{1}{2}(3 + 2\alpha)P_i + (1 + \alpha)P_M, \text{ since } P_i = 2P_{O_2}. \quad (2)$$

$$\text{Now } K = \frac{P_{N_2O_4} + P^1_{N_2O_4}}{(P_{NO_2} + P^1_{NO_2})^2} = \frac{2P_{O_2}(1 - \alpha) + P_M(1 - \alpha)}{(4P_{O_2} + 2\alpha P_M)^2}$$

$$i.e., \quad K = \frac{(1 - \alpha)}{4\alpha^2(2P_{O_2} + P_M)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

By elimination we obtain

$$\alpha^2(4KP_M + 8KP_f + 2) + \alpha - 3 = 0,$$

α being determined, P_i is then obtained from equation 2.

In the same way it can be shown that

$$P - P_i = (\tfrac{1}{2} + \alpha)p + (1 + \alpha)P_M \quad . \quad . \quad . \quad (4)$$

whence, by use of equation 3,

$$\alpha^2(4KP_M - 8K\sqrt{P - P_i} - 2) + \alpha + 1 = 0 \quad . \quad . \quad (5)$$

Equations 4 and 5 enable the values of p to be determined and then the calculation is as before.

The actual mean values of k finally obtained, $37{\cdot}1 \times 10^{-3}$ in the case of oxygen excess and $35{\cdot}6 \times 10^{-3}$ in that of the tetroxide, are in very good agreement with the previous experimental data. The value in the case of the tetroxide is slightly lower, but owing to increased difficulty of manipulation the margin of experimental error is also correspondingly increased.

The effect of dry air was next examined, and the value of k obtained (Experiment 18, $k = 37{\cdot}5 \times 10^{-3}$) also showed no deviation from the previous results. The possibility of impurities such as nitrogen and carbon dioxide exercising a ruling effect on the progress of the reaction was thus put out of the question.

It was considered of interest to examine, also, the effect of moist air, and in Experiment 19 air was admitted straight into the reaction chamber without any preliminary drying or purification. As the value of k obtained seemed rather remarkable, the results are shown in full in Table V.

TABLE V.

Experiment 19 (Temperature = 47°).

Pressure of air admitted = 122·3 mm.

t.	P.	$P-P_t$.	p.	$k\times10^3$.
10	159·8	69·0	54·7	—
20	172·7	81·9	66·3	39·3
30	181·2	90·4	74·0	37·7
40	186·2	95·4	78·9	34·5
50	190·0	99·2	82·5	36·0
Inf.	198·5	—	90·8	—
5	152·3	61·5	48·0	—
15	166·6	75·8	60·6	34·9
25	177·6	86·8	70·6	40·2
35	183·9	93·1	76·5	34·6
45	188·1	97·3	80·7	34·7
			Mean	36·5

When this experiment was undertaken, it was quite expected that the water vapour present would exercise a considerable disturbing effect on the velocity of decomposition, on account of the occurrence of the secondary reaction, $H_2O + N_2O_5 \longrightarrow 2HNO_3$, and on account of the pronounced polarity of the water molecule. On the contrary the velocity of reaction is still unchanged. A possible explanation may lie in the method of calculation of the initial pressure of the pentoxide. The water molecules present would react instantaneously with the nitrogen pentoxide molecules to give nitric acid, after which the dissociation would proceed. The initial pressure of pentoxide calculated would then of necessity be the pressure after this preliminary reaction. Since this initial combination would take place in a shorter time than it took to admit and measure the pressure of the air, it could not be detected on the present apparatus. In any case, however, in this experiment small traces of nitric acid not present in other cases must have been in the reaction vessel during the actual measurements of the rate of decomposition. If then, as seems most likely, the molecules of the acid formed some sort of surface layer on the walls of the vessel, there is obviously here a further argument in favour of the true homogeneity of this reaction.

In order to complete the investigation experiments were performed at a lower temperature with a view to determine the temperature coefficient. The data of two such experiments are summarised in the following table.

TABLE VI.

Temperature = 35·4°.

Expt.	P_f.	P_i.	$k\times10^3$.
21	320·0	172·6	6·82
23	300·2	165·3	7·40
		Mean	7·11

The value calculated for the same temperature from the data of Daniels and Johnston, namely, $k = 7{\cdot}71 \times 10^{-3}$, is seen to be very close to the above mean value. The extremely large value of the temperature coefficient, namely, an increase of over 300% in the velocity for a 10° rise in temperature, seems to afford additional evidence in support of the view that catalysis by the walls of the vessel is not a factor in determining the reaction velocity.

In the next series of experiments undertaken, an attempt was made to repeat the results of Daniels, Wulf, and Karrer (*loc. cit.*). On this work had been based their conclusion that the nitrogen tetroxide is the autocatalytic agent in the reaction. They had found that the initial rate of decomposition of the pentoxide when perfectly free from all traces of tetroxide was extremely slow. The complete elimination of nitrogen tetroxide was ensured by the presence of a small excess of ozone, and the appearance of brown fumes due to the commencement of the dissociation of the pentoxide was then watched for. The results of one experiment only are quoted, and in this case the gaseous pentoxide was kept for 280 minutes before the brown coloration was noted, during 75 minutes of which time the temperature of the vessel was maintained at 80°. It can be calculated that at this temperature the brown fumes should have appeared in about 0·002 second, assuming the decomposition of the pentoxide to take place in accordance with the results of Daniels and Johnston (*loc. cit.*).

In the first case a qualitative experiment was made on the same lines as before, with the difference that now dry ozonised oxygen was admitted. The ozone content of the mixture was in all the following cases between 3 and 3·5% by volume and was measured in the usual manner by absorption in neutral potassium iodide solution, acidification, and subsequent titration with sodium thiosulphate solution. Since the oxidation of nitrogen tetroxide to nitrogen pentoxide by ozone is instantaneous (Wulf, Daniels, and Karrer, *loc. cit.*, p. 2398), the admission of excess ozone ensured the presence of pure pentoxide only and consequently it was expected to find a definite point of inflection on the velocity curve, where the pentoxide began to decompose uniformly. No such effect was observed, all the points lying on a perfectly smooth curve. As this was the case, colorimetric determinations were undertaken similar in nature to those of the above authors, the main difference being that here the starting point was nitrogen pentoxide with a very small percentage of tetroxide present, instead of pure tetroxide. The results of several such determinations are presented in Table VII.

A spectroscopic method of determining the first appearance of the

TABLE VII.

No. 1. Pressure of N_2O_5 = 31·5 mm. Pressure of ozone–oxygen mixture = 519·0 mm.			No. 3. Pressure of N_2O_5 = 38·5 mm. Pressure of O_3–O_2 mixture = 469·0 mm.		
Time (min.).	Temp.	Colour.	Time (min.).	Temp.	Colour.
0	15°	Colourless.	0	20°	Colourless.
75	15	Colourless.	75	20	Colourless.
80	Immersed in thermostat, at 47		79	Heated to 47	—
90	47	Trace of colour.	81	47	Dense brown.
100	47	Dense brown.			

No.	Temp.	$P(N_2O_5)$.	$P(O_3$–O_2 mixture).	Time of colour change.
2	47°	64·0 mm.	469·0	After 3 min.
5	60	47·5 ,,	308·5	Instantaneous.
6	20	47·0 ,,	308·5	After 160—170 min.
7	33	52·0 ,,	410·0	After 9 min.
8	35	23·5 ,,	215·0	After 7 min.

nitrogen tetroxide was tried, but direct vision by the naked eye of the vessel suitably illuminated was found to be quite as sensitive. It will be seen that in no experiment was the effect noted by Daniels, Wulf, and Karrer observed. The appearance of the brown fumes at 80° was to all intents and purposes instantaneous in every case, whilst, wherever tested, the rate of pressure increase was found to be uniformly smooth.

An endeavour to substantiate the accuracy of the above results proved entirely successful. This was done in the following manner. A system of bulbs as shown in diagram 2 was attached to the apparatus. The whole was first carefully evacuated, tap T_6 was then closed, and the pentoxide admitted to a known pressure. A large excess of ozonised oxygen was then allowed to flow in and the final pressure noted. Any tetroxide present would at once be oxidised to pentoxide. Tap T_5 was then closed and the tube quickly sealed at S and drawn off. An estimation of the excess ozone in bulb B was immediately carried out. After absorption of the nitrogen pentoxide in water, the remaining gases were driven into bulb A, where the ozone content could be measured in the usual manner. From a knowledge of the volume of bulb B, and of the actual amount of ozone present, the partial pressure of the ozone in the mixture could be calculated, and hence the concentration of the excess ozone in the actual vessel wherein the coloration experiment was being conducted could be determined.

In the first case investigated, the actual amount of ozone determined was 0·00072 g. The volume of the bulb was 94 c.c., whence the partial pressure of the excess ozone is found to be 2·72 mm. Now, assuming the reaction proceeds unhindered by ozone and neg-

lecting the decomposition of the ozone itself, a calculation can be made of the time which must elapse before the appearance of the brown fumes. The time required for the decomposition of the excess ozone on the assumption that it is continuously oxidising the tetroxide that is formed is given by

$$t = P_{O_3}/k \,.\, P_{N_2O_5},$$

where k is the velocity coefficient of the decay of nitrogen pentoxide at the temperature in question. Two accurate coloration experiments were conducted with the above excess of ozone, the first at 47°, the second at 18·5°, and the times that elapsed before the appearance of the brown colour due to free tetroxide were 2 min. and 95 min. respectively. From the known initial concentration of ozone in the inflowing ozonised oxygen, the amount of tetroxide present as impurity in the nitrogen pentoxide was calculated and hence the true initial pressure of the pentoxide was found to be 35 mm.

From the above formula,

$$\text{at } 47°,\ t = 2{\cdot}72/35 \times 0{\cdot}037 = 2{\cdot}1 \text{ min.}$$
$$\text{while at } 20°,\ t = 2{\cdot}72/35 \times 0{\cdot}0008 = \text{approx. } 97 \text{ min.}$$

Two other similar experiments were conducted, both giving entirely concordant results. It may be mentioned that in one case where the partial pressure of the excess ozone was 28·2 mm. and the initial pressure of nitrogen pentoxide only 37 mm., whilst no colour change was observed after 92 min. at 19°, on raising the temperature suddenly to 80°, the change was immediate. The same type of calculation may be applied to all the previous results contained in Table VII, although only approximate answers can be obtained, since the concentration of the excess ozone was by no means accurately known. No obvious disagreement will, however, be found in any of the cases examined.

An explanation of the effect observed by Wulf, Daniels, and Karrer (*loc. cit.*) has been sought, but so far with no success. Since extreme care was taken both in the preparation of the nitrogen pentoxide and in the purification of the oxygen, as well as in the drying of these gases, the possibility of the presence of some positive catalyst in the present experiments which was lacking in those of the above-mentioned authors seems extremely remote. The question of the presence of water vapour might be raised, but to ensure its absence as far as possible in every case the reaction bulb was baked out under vacuum and all the entering gases were passed through phosphorus pentoxide drying tubes. Consequently the only water vapour which could have been present must have been that left in

the walls of the reaction vessel, since the removal of every trace from the glass is an extremely difficult matter. Wall effect, however, seems not to be a factor, in so far as the variation of surface area can be regarded as a true criterion of its absence, so it would not be expected that any such residual traces left in the walls would affect the course of the reaction. The large temperature coefficient, found both in the former and in the present work, also lends support to the view that the velocity of a true chemical reaction is being measured. Indeed, in view of the above results, in the case of the thermal decomposition of nitrogen pentoxide, evidence in support of the autocatalysis by traces of nitrogen tetroxide is entirely lacking. All the data now available seem to render more than probable the assumption that this reaction is really homogeneous and non-catalytic. Some importance may also be attached to the fact that no inhibitor of the reaction has yet been found. Indeed, the constancy of the values of k under very different conditions seems remarkable in the extreme.

If it is correct to assume the absence of any autocatalytic effect, an assumption which seems to be well supported by the experimental data, questions of great interest arise as to the mechanism of the reaction. What, for example, is the primary cause of the activation of the molecules and how is the supply of active molecules then maintained? Is it a kinetic collision effect as postulated in the "hot molecule" theory of Christiansen and Kramers (*loc. cit.*), or is there communication of energy by collisions of the second kind as in the phenomena recently described in the work of Cario and Franck (*Z. Physik*, 1922, **11**, 161)? It is hoped that considerable information on these lines may be obtained from a study of the reaction velocity at low pressures, where the mean free path of the molecules is large. Investigations of this nature are now being conducted in collaboration with Dr. Rideal.

In conclusion, I wish to express my very best thanks to Sir J. J. Thomson for his continued helpful criticism and advice, to Dr. Ludlam for details of the method of construction of the all-glass pressure gauge, and to the Department of Scientific and Industrial Research for a maintenance grant which rendered this research possible.

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[*Received, December 17th*, 1924.]

XCVI.—*Limits for the Propagation of Flame in Inflammable Gas–Air Mixtures. Part III. The Effect of Temperature on the Limits.*

By Albert Greville White.

In many industrial processes inflammable gas–air mixtures are used at elevated temperatures. A knowledge of the effect of initial temperature on the limits for the propagation of flame in gas–air mixtures is thus of importance, and this work was initiated partly to procure such knowledge, and partly in an attempt to secure some information as to the mode of propagation of flame in limit mixtures.

Since a flame travelling along a tube containing an inflammable gas mixture must bring each layer in turn to a temperature at which it can burn, the ignition temperature of a gas might be expected to affect materially the limiting quantities which could be mixed with air to give a mixture which will propagate flame. Bunsen, in his "Gasometriche Methoden," attempted to deduce certain ignition temperatures from determinations of limits for the propagation of flame on the assumptions that the heat liberated in the burning layer is all transferred to the next unburnt layer, and is just sufficient to raise the latter to its ignition temperature. Ignition temperatures experimentally determined differed considerably from Bunsen's values, and more recent attempts to calculate limits from ignition temperatures on similar lines have also proved unsatisfactory, as may be seen from the figures given in Table I. The lower-limit values there given were determined for downward propagation (Part I and J., 1922, **121**, 1244), in order to eliminate convection effects as far as possible.

Table I.

Limits for the propagation of flame in various combustible–air mixtures.

Combustible.	Net calorific value.	Ignition temp.	Lower limit. Expt. (*E*).	Calc. (*C*).	*R*=*E*/*C*.
Methane	190	700°	5·95	2·55	2·3
Hydrogen	57	585	8·8	6·9	1·28
Ethyl ether	604	227	1·85	0·235	7·9
Carbon monoxide ...	68	651	15·3	6·5	2·35
Acetylene	301	429	2·78	0·94	3·0
Ethylene	315	543	3·33	1·16	2·9

The values used for the specific heats of methane, ether, acetylene, and ethylene were 15·2, 31·7, 11·5 and 13·0 Cals. respectively. For nitrogen, carbon dioxide, and steam, the values were those of

Holborn and Henning (*Ann. Phys.*, 1905, [iv], **18**, 739; 1907, [iv], **23**, 809), whilst for the other gases those of Lewis and Randall (*J. Amer. Chem. Soc.*, 1912, **34**, 1128) were taken. All the figures were for constant pressure and no correction has been made for loss of heat. The ignition temperatures used are those of Dixon and Coward (J., 1909, **95**, 514), except for ether, for which the mean value given by Tizard and Pye (*Phil. Mag.*, 1922, [vi], **44**, 79) has been utilised.

The large ratios of the two limits in Table I suggest that only a small part of the heat given out by a burning layer is used to heat the next layer to its ignition temperature, whilst the variations in the ratios indicate that the percentage so used differs greatly for different combustibles. The heat not so used may be lost (1) to the tube containing the gas, (2) to the bulk of the unburnt gas, (3) to the burnt gas; but in most cases there would appear to be much more heat left than would be necessary to raise the unburnt layer to its ignition temperature. The great conductivity for heat of hydrogen might be advanced to account for the low value of the ratio in this case, but in the other cases, where the conductivities of the lower-limit mixtures, and the calorific values per unit volume, should not differ much, the flame temperatures, the heat losses, and the rate at which the heat is transmitted to the nearest unburnt layer should be similar, so that there should be a rough parallelism between the ignition temperatures and the calorific values at the lower limit. Since this is not the case, it appears that the ignition temperature of the gas has little direct connexion with the propagation of flame in the lower-limit mixture, and that the effective ignition temperature during the propagation of flame may often be much greater than that ordinarily determined (compare J., 1922, **121**, 1244).

The question is obviously important. A simple method of procuring information appeared to be that of determining the limits of gas mixtures at various temperatures. The method depends on the assumption that the ignition temperature of a gas mixture at concentrations similar to those present in a lower-limit mixture does not vary much with the concentration of the inflammable gas. This assumption has not been proved to hold generally, but it has been shown to hold for hydrogen–oxygen mixtures by Dixon and Crofts (J., 1914, **105**, 2036), and for methane–air mixtures by Wheeler (*Trans. Inst. Mining Eng.*, **63**, Part I, 14), whilst Tizard and Pye (*loc. cit.*) believe that the ignition temperature changes little throughout the whole range for heptane–air. If the ignition temperature functioning during propagation were high, the change to be expected in the limit when the initial temperature of the gas

mixture is changed by a definite amount would be less than if the ignition temperature were low.

Published Information Available.—The amount of work that has been carried out on the effect of the initial temperature of a gas–air mixture on its limits for the propagation of flame is comparatively small, and the main portion deals only with methane–air mixtures. The communications dealing with the subject in any detail are referred to below.

Author.	Reference.	Mixtures considered.
Bunte and Roszkowski.	*J. Gas Wasser.*, 1890, 491, 524, 535, 553.	Methane, hydrogen, carbon monoxide and illuminating gas with oxygen, air and an artificial atmosphere.
Roszkowski.	*Z. physikal. Chem.*, 1891, **7**, 485.	
Le Chatelier and Boudouard.	*Compt. rend.*, 1898, **126**, 1344.	Carbon monoxide and air.
Taffanel and Le Floch.	*Ibid.*, 1913, **157**, 595.	Methane and air.
Burrell and Robertson.	U.S. Bureau of Mines, Tech. Paper 121, 1916.	Methane and air.
Mason and Wheeler.	J., 1918, **113**, 45.	Methane and air.
White.	J., 1922, **121**, 1688.	Ammonia with air and oxygen.
Berl and Fischer.	*Z. Elektrochem.*, 1924, **30**, 29.	Carbon monoxide, hydrogen, methane, acetylene, ethylene, and certain organic vapours with air.

The most ambitious of the older programmes was attempted by Bunte and Roszkowski, who made use of a small vessel. Their results would tend to show that in many cases the limits change little when the initial temperature of the gas is varied from 15° to 300°. This is not a result to be expected on theoretical grounds, and is almost certainly due to a change in the composition of the gas mixture due to an over-long preliminary heating.

The experiments of Le Chatelier and Boudouard were carried out in a tube, and showed that there was an important change in the limit of carbon monoxide–air when the initial temperature was increased. Taffanel and Le Floch, and also Mason and Wheeler, used a tube. The dimensions are not given by the earlier workers but that used by Mason and Wheeler was 20 mm. in diameter and 15 cm. long. The English workers dealt with propagation downwards, but allowed the flame to travel up a vertical limb connected to the bottom of the limit tube proper in order to ascertain easily when propagation occurred. Burrell and Robertson used as limit vessel an explosion pipette, and decided whether the mixture was above or below the limit by analysing the gas left in the pipette after sparking.

The author's work with ammonia mixtures was carried out

with tubes considerably larger than most of those previously utilised for such experiments, the object being to obtain more accurate results. The work recently published by Berl and Fischer is said to be on explosion limits, and the experimental conditions were not conducive to accurate work on limits for the propagation of flame. The explosion vessel was a glass pipette of unspecified dimensions, but was small enough for a powerful spark to give limit results markedly different from those given by normal sparking. Two sets of results were taken at each temperature, the mixture remaining in the heated pipette for 1 minute in the one series, and for 2 minutes in the other, before firing. The results were in agreement over the whole temperature range only for hydrogen and methane at both limits, and for acetone at the lower limit; definite results were not obtained for either acetylene or ethylene at the upper limit. The lack of agreement between the two sets of results for carbon monoxide, ethylene, and acetylene indicates that preliminary combustion of these mixtures took place during the second minute, so that the results given for these gases for 1 minute's heating should be regarded with suspicion.

Experimental.

The method previously utilised for ammonia was employed, and the aim was accuracy at moderate temperatures rather than less trustworthy results at higher temperatures. As there was considerably more danger of " baking " with the gases now used than with ammonia, the heating of the gas mixtures was speeded up by using a tube 25 mm. in diameter. The tube was of the same length as before — 1·5 metres. Except where otherwise specified, the experimental details were precisely as previously described. An accuracy of 1% on the inflammable gas used was aimed at. All the results are for downward propagation, except where otherwise specified.

To obtain more uniform heating near the ends of the furnace than was possible during the former experiments, special auxiliary heating coils were wound. These proved quite successful, and reduced the variation of temperature along the furnace from 20° to less than 10° at the highest temperature used. The gas mixture was made up in a 6-litre glass aspirator, and the amount of mercury introduced into this before filling the tube from it was carefully adjusted, so that there should be no excess of pressure over that of the atmosphere when once the gas in the tube had attained the furnace temperature. This was done by preliminary trial, as a small portion of the tube projected from the furnace and was thus at a temperature that was not known accurately. A very large

TABLE II.

Showing the ranges that will propagate flame at various temperatures for mixtures of various gases with air in tubes 25 mm. in diameter, and also the results of determinations for methane in tubes 18 mm. in diameter.

	Ranges that will propagate flame in						
			CH_4.				
Temp.	H_2.	CO.	25 mm.	18 mm.	C_2H_4.	C_2H_2.	n-C_5H_{12}.
	9·40	16·3	6·30	—	3·45	2·90	1·53
17°±3°	to	to	to	to	to	to	to
	71·5	70·0	12·9	12·7	13·7	55·0	4·50
	9·2	15·7	6·20	—	3·35	2·83	1·50
50	to	to	to	to	to	to	to
	—	—	—	—	—	59·0	—
	8·8	14·8	5·95	—	3·20	2·68	1·44
100	to	to	to	to	to	to	to
	73·5	71·5	13·7	13·3	14·1	65·0	4·75
	8·3	14·2	5·75	—	3·10	2·52	1·39
150	to	to	to	to	to	to	to
	—	—	14·1	—	—	73·0	4·90
	7·9	13·5	5·50	—	2·95	2·39	1·34
200	to	to	to	to	to	to	to
	76·0	73·0	14·6	14·1	14·9	81·0 *	5·05
	7·5	12·9	5·30	—	2·85	2·30	1·30
250	to	to	to	to	to	to	to
	—	—	—	—	15·7	—	—
	7·1	12·4	5·10	—	2·75	2·19	1·22
300	to	to	to	to	to	to	to
	79·0	75·0	15·5	15·0	17·9	—	5·35
	6·7	12·0	4·90	—	2·60		
350	to	to	to	to	to		
	—	—	—	—	—		
	6·3	11·4	4·80	—	2·50		
400	to	to	to	to	to		
	81·5	77·5	16·6	15·8	—		
			4·55				
450			to				
			—				

* This value is known to be somewhat low, but was the highest value obtainable under the experimental conditions. For this result, the gas mixture was in the tube 2 seconds before ignition. Allowing the gas mixture to remain an extra 2 seconds in the tube before ignition gave a still lower figure for the limit.

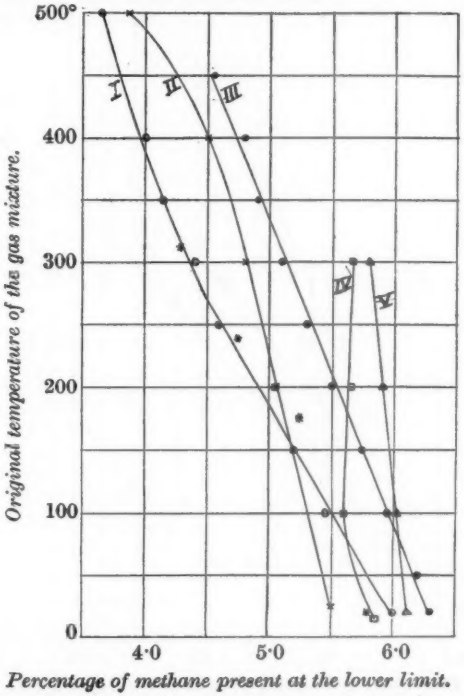
stopcock was introduced between the tube and the bottle, so that the filling of the tube occupied the minimum of time. The time between the opening of the cock and the firing of the mixture was finally reduced to a little over 2 seconds. Whenever there was any doubt as to the condition of a mixture at the time of firing, the result was checked by firing the same mixture, allowing it to remain an extra 2 seconds in the tube before ignition. The thermocouple was removed from the tube immediately before firing, but another couple, placed between the tube and the furnace wall, registered

any change occurring later. The result of a trial was determined visually through an observation hole in the asbestos packing at one end of the tube. Owing to the distance between the tube and the wall of the furnace, after practice it was comparatively easy to follow the progress of a flame down the tube.

The inflammable gases used were prepared as described in Part I.

FIG. 1.

Showing the lower-limit values for the propagation of flame in methane–air mixtures obtained by various workers. No curve is drawn through the results of Taffanel and Le Floch, which are shown by asterisks.



I *Mason and Wheeler.* II *Burrell and Robertson.* III *White.* IV *Roszkowski.* V *Berl and Fischer.*

As previously noted with ammonia–air, whenever preliminary "baking" of a mixture took place at a certain temperature, the effect was far more serious at the upper than at the lower limit. All percentages quoted are percentages by volume.

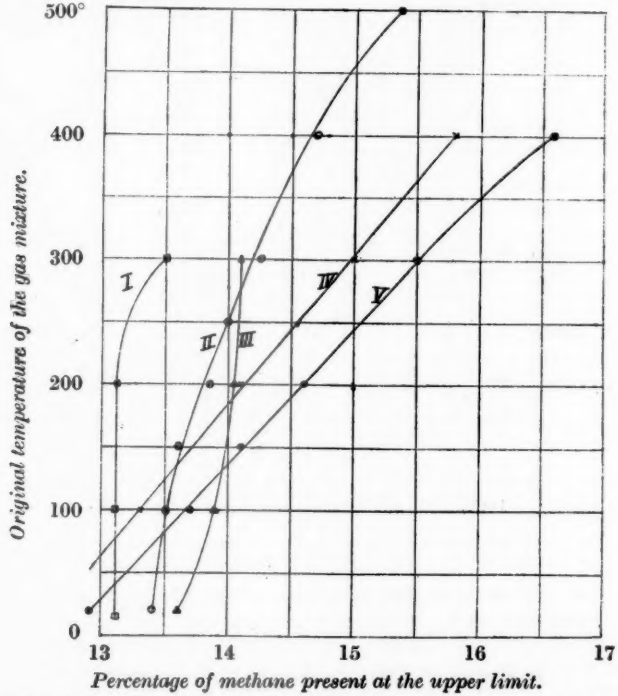
Results.—The results obtained are given in Table II.

A comparison of the author's results with those of other workers is best made by means of Figs. 1 to 4. From the point of view of such a comparison, the absolute value obtained for the limit

at the ordinary temperature is of little account, and it is the slope and general form of the curves that are important. The lower-limit results obtainable for methane (Fig. 1) show that the values of Roszkowski and of Berl and Fischer, who used small vessels and prolonged heating of the gas mixture, indicate a very much smaller fall in the value of the limit with rise of temperature than the results of the other workers. The results of Roszkowski even

FIG. 2.

Showing the upper-limit results for the propagation of flame in methane–air mixtures determined by various workers.



I *Roszkowski.* II *Mason and Wheeler.* III *Berl and Fischer.* IV *White* 18 *mm.* V *White* 25 *mm.*

indicate an increase in the value of the limit when the temperature of the gas mixture is increased from 100° to 300°, and it is certain that both sets of results are in error. The results of Taffanel, of Mason and Wheeler, and of Burrell and Robertson all agree fairly well. The author's results, lying along a straight line, might almost be the mean of those of the American and the English observers. The upper-limit results (Fig. 2) differ considerably from one observer to another. The results of Roszkowski and of Berl and

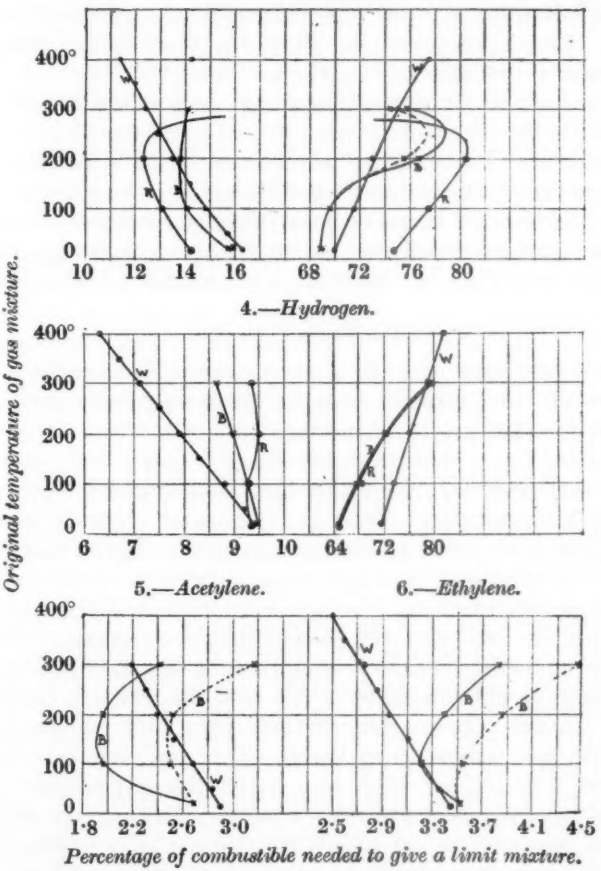
Fischer, regarded as limits for the propagation of flame, again appear to be at fault, as the relative values of some of their figures are improbable in the extreme. There is in this case a serious

FIGS. 3, 4, 5, 6.

Showing the results of various workers for the effect of temperature on the limits of carbon monoxide, hydrogen, acetylene, and ethylene when mixed with air.

The results of Le Chatelier and Boudouard for carbon monoxide are shown by asterisks. The dotted curves for Berl and Fischer show results of experiments in which the mixture was kept at the required temperature for 2 minutes, instead of the usual 1 minute.

R = Roszkowski. B = Berl and Fischer. W = White.



discrepancy between the values now found and those of Mason and Wheeler, as when the initial temperature of the gas mixture is changed from about 20° to 400°, the percentage increase is in

one case about three times that in the other. As the limit vessel used by Mason and Wheeler for their experiments was only 20 mm. in diameter, further determinations were made in a tube having an internal diameter of 18 mm., but a length of 1·5 metres. The slope of the temperature–limit curve is decreased by decreasing the diameter of the tube used as limit vessel, but the effect of diameter alone is not sufficient to account for the difference between the two sets of results. Under the conditions used in this work, horizontal propagation gives results differing only slightly from those for downward propagation. Thus the upper limit for methane in air increased from 12·9 to 15·7% for horizontal propagation when the initial temperature of the mixture was increased from 18° to 300°. The increase in the limit for downward propagation under the same conditions was from 12·9 to 15·5%.

Figs. 3—6 show the present results in comparison with those of Berl and Fischer, Roszkowski, and of Le Chatelier and Boudouard. In no single case do the older results agree with those now determined, and in only one instance, that of the upper limit for hydrogen, can any two sets of them be said to agree amongst themselves. Such discrepancies would not be surprising at very high temperatures, but here they are often large for results between 15° and 100°.

Discussion of Results.

At the lower limit, for all gases except carbon monoxide the present results give straight lines for the temperature–limit curve, and even for this gas the departure from the linear form is not great. At the upper limit the same thing is nearly true, except for ethylene and acetylene, for which the limits increase very rapidly at higher temperatures. Mason and Wheeler observed a similar phenomenon in the case of methane at high temperatures. They seemed to think that at the higher temperatures the results obtained did not properly represent the upper limit for self-propagation in *methane* and air, and suggested the possibility of the early formation of carbon monoxide and hydrogen (both gases having very high upper limits of inflammability). To test this theory, the author exposed ethylene upper-limit mixtures to a high temperature in limit tubes for various short times. The results were not quite conclusive, but did not seem to support this explanation of the high limit results. The difference observed with carbon monoxide at 400° is much too small to settle the question, as these upper-limit results were only decided to the nearest 0·5%. Experiments with this gas at higher temperatures might enable a decision to be made, as it certainly cannot give rise to any known compounds except carbon dioxide under the experimental conditions obtaining.

It has been shown (J., 1922, **121**, 1688) that at the lower limit in ammonia–air and –oxygen mixtures the theoretical flame temperature remains practically constant for a range extending from the ordinary temperature to 450°. The same calculations have been made for the gases now examined. The results given in Table III show that in all but two cases the theoretical flame temperature remains much the same throughout the temperature range utilised. There appears to be some slight tendency for the flame temperature to decrease as the initial temperature of the mixture is increased, but this increase is little greater than the experimental variations. Of the two exceptions, one is only an exception below 100°—at and above that temperature the results for carbon monoxide agree with those for the majority. In the case of hydrogen, however, the flame temperature increases steadily with the initial temperature, the increase over the whole range being far outside any possible manipulative experimental error. We thus see that at the lower limit the results for six out of the seven gases examined conform approximately to a simple rule, so that from the practical point of view it becomes easy to make an allowance for the effect of temperature on the lower limit. Of its significance on the theoretical side it need only be said that, once granted the required premises as to the rate of variation of the ignition temperature near the lower limit, it appears to do away with any idea that the ordinary ignition temperature of a gas can have any direct connexion with the propagation of flame in it.

TABLE III.

Showing the theoretical flame temperatures attained at the lower limit, and in some cases at the upper limit, for the propagation of flame in various gas–air mixtures at different temperatures up to 450°.

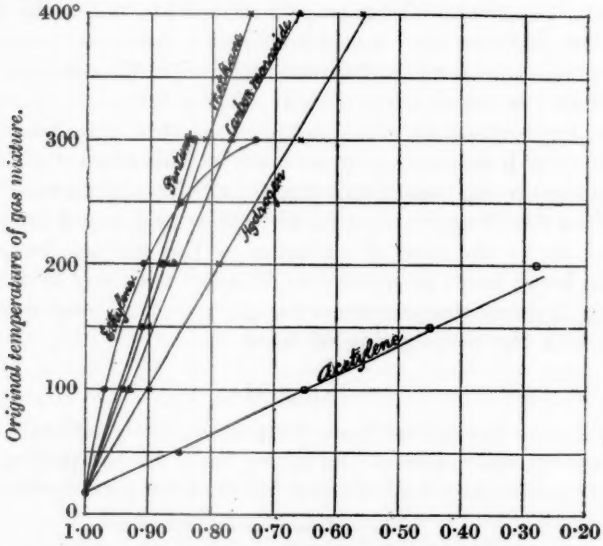
	Theoretical flame temperature.							
Initial temp. of gas mixture.	Hydrogen. Lower limit.	Hydrogen. Upper limit.	Carbon monoxide. Lower limit.	Carbon monoxide. Upper limit.	Methane. Lower limit.	Ethylene. Lower limit.	Acetylene. Lower limit.	*n*-Pentane. Lower limit.
17°±3°	815°	980°	1490°	1120°	1535°	1420°	1195°	1490°
50	820		1465		1530	1405	1195	1485
100	825	970	1435	1130	1515	1390	1180	1475
150	830		1425		1515	1395	1165	1475
200	845	975	1410	1160	1505	1385	1160	1475
250	860		1405		1505	1390	1170	1485
300	875	970	1405	1170	1505	1400	1175	1465
350	890		1415		1505	1390		
400	900	980	1410	1170	1530	1395		
450					1520			

The upper-limit results show that of the two gases available for calculation one agrees with ammonia in showing a theoretical flame

temperature that increases with increase of initial gas temperature, whilst the other shows almost identical flame temperatures under the same conditions. Owing to our ignorance of the exact products of combustion at the upper limit, in many cases it is not possible to find out how the theoretical flame temperature or calorific value at this limit is affected by rise of temperature of the original mixture. For upper-limit results, therefore, Fig. 7 has been drawn, showing how the oxygen–combustible ratio decreases as the initial temperature of the limit mixture is increased, the ratio at the

FIG. 7.

Showing the oxygen/combustible ratio for the upper-limit mixtures of various gases and air at various temperatures, the ratio at the ordinary temperature being taken as unity.



ordinary temperature being taken as unity. The ratios determined seem to lie on approximately straight lines for all the gases examined except ethylene, in which case a small original fall rapidly increases as the temperature rises. The decrease in ratio appears to be far more rapid for acetylene than for the other gases, whilst that for methane appears to be much the same as that for pentane.

The lower-limit results may also be examined from a slightly different angle.

The figures given in Table IV are taken from, or calculated from values given in, Tables I and II. The new table shows the calorific values of the lower-limit mixtures both at the ordinary temperature

TABLE IV.

Showing the calorific values of certain lower-limit mixtures at the ordinary and at a much higher temperature, and certain relations between these and the heat needed to bring the lower-limit mixture up to its ignition temperature and to the temperature of the second limit experiment.

Gas used.	Calorific value of lower limit mixture at 17°±3°. C_1.	Calorific value of lower limit mixture at 400°.* C_2.	C_1-C_2.	Heat in Cals. needed to bring mixture from 17° to 400°.* C_3.	$\frac{100(C_1-C_2-C_3)}{C_1}$.	$\frac{100(R-1)}{R}$. See Table I.	Ignition temperature.
Hydrogen .	536	359	177	261	−16	22	585°
Carbon monoxide .	1108	775	333	261	+6	57	651
Methane ...	1197	912	285	270	+1	57	700
Ethylene ...	1087	788	299	265	+3	66	543
Acetylene ...	873	659	214	193	+2	67	429
Pentane ...	1193	951	242	199	+4	—	400?

* 300° was the temperature used in both these cases for acetylene and for pentane. The ignition temperature of pentane is given as 400°, but this is merely a rough estimate based on the values of Dixon and Coward for methane and for ethane (575°), and on that of Tizard and Pye for heptane (300°).

and at a chosen high temperature. The amount of heat needed to bring the lower-limit mixtures to these temperatures is also given, and it is easily seen that by subtracting this from the difference between the two former values we get the heat saved by determining the limit at the higher temperature. This is the portion of the heat unutilised for heating up the unburnt mixture at the ordinary temperature which is made use of at the higher temperature. If this higher temperature is considerably nearer the ignition temperature of the limit mixture than the ordinary temperature, the heat thus saved should form a fair proportion of the total heat lost at the ordinary temperature, as all losses should be cut down by the use of a higher initial temperature. The fifth column shows the heat saved at the higher temperature, whilst the sixth shows the total heat lost at the ordinary temperature, both being given as a percentage of the calorific value of the limit mixture at the ordinary temperature. In only one case—that of hydrogen—does the proportion of the total heat saved become significant. For hydrogen, not only has the heat saved a relatively greater value than in the other cases, but it is of a different sign, showing a considerably greater loss of heat at 400° than at the ordinary temperature. The ordinary ignition temperature theory thus seems to break down in this case. The same conclusion can

be drawn from the heat lost at various temperatures for the other gases, so that all the evidence obtained during the course of this work seems to show that the ordinary ignition temperature is not the effective ignition temperature during the propagation of flame.

Summary.

Limits for the propagation of flame downward have been determined in tubes 25 mm. in diameter and 1·5 metres long at various temperatures up to 400°, where possible, for mixtures of hydrogen, carbon monoxide, methane, ethylene, acetylene, and pentane with air. The results obtained agree reasonably well with some of the moderately recent results for the lower limits of methane in air, but do not accord with any of the upper-limit results in the literature. Incidentally, the latter do not agree amongst themselves.

The temperature–lower-limit curves obtained are very nearly straight lines, the limit figure falling by from 6 to about 8% per 100°. Similar curves for the upper limits are also straight lines in certain cases, but for ethylene and acetylene the upper-limit figures increase very rapidly at the higher temperatures.

Calculation showed that at the lower limit, for all the gases except hydrogen the theoretical flame temperature remained approximately the same throughout the whole temperature range. A consideration of these values and of the value of the limits at various temperatures is considered to support the view that the ignition temperature as ordinarily determined has little to do with the propagation of flame.

Determinations of upper limits for the propagation of flame in methane–air in 25 mm. and in 18 mm. tubes showed that the limits determined in the narrower tube increased less rapidly with temperature than did those determined in the wider tube. For the same gas mixture, much the same results were obtained for horizontal as for downward propagation.

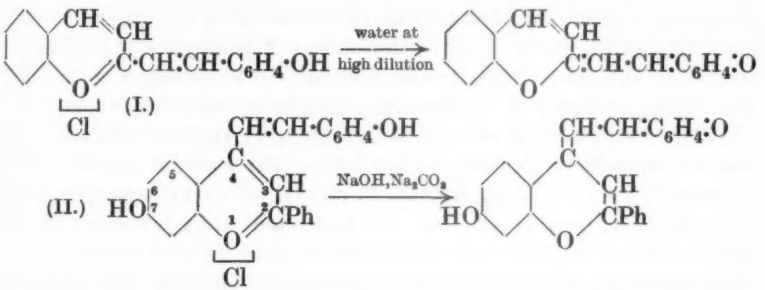
I wish to thank Messrs. Nobel Industries, Ltd., and particularly Mr. W. Rintoul, Manager of the Research Section, for facilities accorded me for carrying out this work.

THE NOBEL LABORATORIES, ARDEER. [*Received, December 9th,* 1924.]

XCVII.—*Styrylbenzopyrylium Salts. Part IV. γ-Styryl Derivatives of 5 : 7-Dihydroxy- and 5 : 7-Dimethoxy-2-phenyl-4-methylbenzopyrylium Chloride.*

By George Hugh Walker and Isidor Morris Heilbron.

It was shown in Part III (Buck and Heilbron, J., 1923, **123**, 2521) that in addition to α-styrylbenzopyrylium salts, γ-styryl derivatives could readily be prepared by the condensation of 7-hydroxy-2-phenyl-4-methylbenzopyrylium chloride with aromatic aldehydes. These salts differed from the α-class (J., 1922, **121**, 1198) in having a free hydroxyl group in position 7. In both series, the formation of quinonoid anhydro-bases was noted in all chlorides containing a *p*-hydroxyl group in the styryl residue, but whereas with 4′-hydroxy-2-styrylbenzopyrylium chloride (I) the change was brought about on dilution with water alone, this only occurred with 4′ : 7-dihydroxy-2-phenyl-4-styrylbenzopyrylium chloride (II) in presence of dilute sodium hydroxide or sodium carbonate solution.



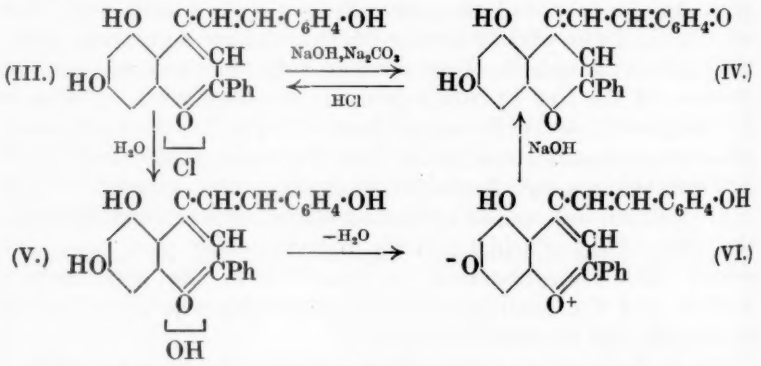
With the object of studying the effect of an additional hydroxyl group on the colour of the γ-styrylbenzopyrylium salts and their solutions and also of determining whether the non-formation of the blue quinonoid anhydro-base on water dilution was due to the presence of the free hydroxyl group in the 7-position, a series of 5 : 7-dihydroxy-γ-styrylbenzopyrylium chlorides has been prepared, and their properties compared with the analogously constituted 5 : 7-dimethoxy-γ-styrylbenzopyrylium salts. The general method of preparation was similar to that employed by Buck and Heilbron (*loc. cit.*). Phloroglucinol and its dimethyl ether were each condensed with benzoylacetone as described in the experimental portion, and the resulting benzopyrylium chlorides then further condensed with aromatic aldehydes.

The 5 : 7-dihydroxy-γ-styrylbenzopyrylium chlorides are highly-coloured, crystalline salts which show the usual behaviour of members of this series in that they sinter and melt with decomposi-

tion. They are characterised by their sparing solubility in comparison with the corresponding members of the 7-hydroxy series (formula II). The effect of the hydroxyl group in the 5-position is otherwise by no means pronounced, but there is an unexpected noticeable decrease in colour both of the dry salts and of their solutions in alcohol. As with the salts of the 7-hydroxy-γ-styryl series, a deep blue or bluish-violet colour is developed on addition of a few drops of dilute sodium hydroxide or sodium carbonate solution to the red, aqueous alcoholic solution of all chlorides containing a *p*-hydroxy-group in the styryl residue. In the case of the *p*-methoxy-analogues, the red colour remains unimpaired, as quinonoid formation is impossible and isomerisation to the colourless carbinol bases does not occur in this series.

The 5 : 7-dimethoxy-2-phenyl-4-styrylbenzopyrylium chlorides closely resemble the corresponding hydroxy-salts, but their solutions in alcohol are considerably deeper in colour, indicative of the increased auxochromic influence of the methoxyl groups, and they are very much more soluble in alcohol and glacial acetic acid. One of the most interesting compounds of this series is the green, crystalline 5 : 7-dimethoxy-4′-dimethylamino-2-phenyl-4-styrylbenzopyrylium chloride, which is the first salt to be isolated containing the $-NMe_2$ grouping in the free state in a form suitable for analysis.

Their chief point of interest lies in the fact that on dilution with water they behave similarly to the salts of the α-styryl series. Thus, whereas 4′ : 5 : 7-trihydroxy-2-phenyl-4-styrylbenzopyrylium chloride (III) only passes into the quinonoid anhydro-base (IV) on addition of alkali, the same change takes place with 5 : 7-dimethoxy-4′-hydroxy-2-phenyl-4-styrylbenzopyrylium chloride on dilution with water alone.



It would thus appear that the presence of the 7-hydroxyl group is undoubtedly the retarding influence in the rearrangement to

quinonoid anhydro-base. This may possibly be due to the colour base (V), which is doubtless formed on hydrolysis of III, passing, without change of colour, into the more stable betaine (VI), which is immediately transformed by alkali into the quinonoid base (IV).

EXPERIMENTAL.

5 : 7-*Dihydroxy*-2-*phenyl*-4-*methylbenzopyrylium chloride*, orange-red needles, was prepared by a slight modification of Bülow and Wagner's method (*Ber.*, 1901, **34**, 1782), 80% formic acid being employed with advantage as solvent in place of glacial acetic acid. The double *ferrichloride* separates from glacial acetic acid in presence of dry hydrogen chloride in orange-yellow needles. It contains 1 molecule of water, half of which is lost after standing for two months in an exsiccator over concentrated sulphuric acid (Found : C = 41·7; H = 3·1; Fe = 12·2. $C_{16}H_{13}O_3Cl_4Fe,\frac{1}{2}H_2O$ requires C = 41·7; H = 3·0; Fe = 12·1%).

4′ : 5 : 7-*Trihydroxy*-2-*phenyl*-4-*styrylbenzopyrylium Chloride* (III) —5 : 7-Dihydroxy-2-phenyl-4-methylbenzopyrylium chloride (10 g.) and *p*-hydroxybenzaldehyde (5 g.) were boiled under reflux for 2 hours with absolute alcohol (50 c.c.), a stream of dry hydrogen chloride being passed continually into the boiling solution. The resulting reddish-brown powder crystallises from pure formic acid, in which it is only slightly soluble, after saturation with dry hydrogen chloride, in dark brown needles with metallic reflex, m. p. 260° (Found : C = 70·8; H = 4·3. $C_{23}H_{17}O_4Cl$ requires C = 70·3; H = 4·3%).

5 : 7-*Dihydroxy*-4′-*methoxy*-2-*phenyl*-4-*styrylbenzopyrylium chloride*, prepared in a similar manner, separates, on standing in the ice-chest, as a reddish-brown powder. It crystallises best from a mixture of equal parts of glacial acetic acid and formic acid (80%) after saturation with hydrogen chloride, in bluish-red needles, which become crimson over solid sodium hydroxide in an exsiccator. In alcohol the solution is orange, showing an intense green fluorescence which is destroyed on addition of water. Alkali produces no change in colour (Found : C = 70·5; H = 4·5. $C_{24}H_{19}O_4Cl$ requires C = 70·8; H = 4·7%).

5 : 7-*Dihydroxy*-4′-*dimethylamino*-2-*phenyl*-4-*styrylbenzopyrylium Chloride*.—A solution containing the parent chloride (10 g.), *p*-dimethylaminobenzaldehyde (5 g.), and absolute alcohol (50 c.c.) was heated on the water-bath for 1 hour without hydrogen chloride being introduced, owing to the ready formation of the unstable yellow hydrochloride of the salt, which does not separate from solution. After leaving for 24 hours in an ice-chest, the bluish-green, amorphous powder was filtered off. It was only sparingly

soluble in alcohol (greenish-blue colour) and acetone (purple solution), but could not be obtained in crystalline form. The green alcoholic solution changes, on addition of dilute sodium hydroxide solution, into deep blue, excess of the reagent giving a brown, cloudy solution. The double *ferrichloride* separates on boiling the crude chloride (3 g.) with commercial ferric chloride (4 g.) in glacial acetic acid (30 c.c.). It crystallises from boiling acetone, in which it is readily soluble (purple solution), in dark green needles (m. p. 270°). If dry hydrogen chloride is passed into a solution of this iron salt in glacial acetic acid (cooled in ice), golden-yellow needles of the unstable hydrochloride are obtained (Found : C = 51·6; H = 4·1; Fe = 9·8. $C_{25}H_{22}O_3NCl_4Fe$ requires C = 51·5; H = 3·8; Fe = 9·6%).

The *perchlorate*, formed on addition of 20% perchloric acid to an alcoholic solution of the chloride, crystallises in dark green needles, whilst the *diperchlorate*, obtained by treating a suspension of the chloride in glacial acetic acid with 40% perchloric acid, is orange-yellow. These salts were too explosive to admit of analytical data being obtained.

5 : 7 - *Dimethoxy* - 2 - *phenyl* - 4 - *methylbenzopyrylium Chloride.*—Phloroglucinol dimethyl ether (10 g.), prepared according to Robinson's method (J., 1924, **125**, 193), and benzoylacetone (10·5 g.) were heated under reflux with ether (30 c.c.) until solution was complete. The warm solution was saturated with dry hydrogen chloride during 1 hour, refluxed for a further 10 minutes, and allowed to cool in a slow stream of dry hydrogen chloride. After 12 hours, the whole had solidified, and the crude salt was recrystallised from a small quantity of absolute alcohol previously saturated with hydrogen chloride gas, separating in yellow-brown needles, m. p. 180°, readily soluble in water or dilute hydrochloric acid [Found : C = 62·7; H = 5·3; Cl (Carius) = 15·7.

$$C_{18}H_{17}O_3Cl,\tfrac{1}{2}H_2O,\tfrac{1}{2}HCl$$

requires C = 62·8; H = 5·4; Cl = 15·5%). The *ferrichloride*, which separates from an alcoholic mixture of the reactants on saturation with hydrogen chloride gas, forms long, yellow needles from acetone, m. p. 215° (Found : C = 44·6; H = 3·8; Fe = 11·7. $C_{18}H_{17}O_3Cl_4Fe$ requires C = 45·1; H = 3·5; Fe = 11·7%).

5 : 7-*Dimethoxy*-4'-*hydroxy*-2-*phenyl*-4-*styrylbenzopyrylium Chloride.*—A suspension containing the parent chloride (3·2 g.) and *p*-hydroxybenzaldehyde (1·2 g.) in 18 c.c. of absolute alcohol was heated to boiling and saturated with dry hydrogen chloride during ½ hour. After 12 hours, the crude salt was filtered, washed with ether, and crystallised from a mixture of equal volumes of formic acid and glacial acetic acid containing hydrogen chloride. It separated

in glistening, blue-green needles, m. p. 230°, somewhat sparingly soluble in absolute alcohol to a deep red solution which changed to intense blue either on dilution with water or on addition of dilute alkali (Found : C = 71·5; H = 4·7. $C_{25}H_{21}O_4Cl$ requires C = 71·3; H = 5·0%).

The isomeric 5 : 7-*dimethoxy*-2′-*hydroxy*-2-*phenyl*-4-*styrylbenzopyrylium chloride*, prepared in a similar manner, separates from 80 % formic acid in brick-red needles (m. p. 110°) which in moist air tend to resinify. The colour of this salt is characteristic and, unlike the 4′-hydroxy salt, the red alcoholic solution does not change to blue on simple dilution with water, but only on addition of alkali. The blue colour, which is not so intense, gradually fades to light yellow (Found : C = 68·2; H = 5·4. $C_{25}H_{21}O_4Cl,H_2O$ requires C = 68·4; H = 5·2%).

3′ : 5 : 7-*Trimethoxy*-4′-*hydroxy*-2-*phenyl*-4-*styrylbenzopyrylium Chloride*.—This salt separates as a crystalline sludge on treating the parent chloride (3 g.) in absolute alcohol (18 c.c.) with vanillin (11·5 g.) and rapidly saturating the solution with dry hydrogen chloride. It crystallises from 80% formic acid in brownish-black needles with metallic reflex (m. p. 210°). The red alcoholic solution changes to deep blue on dilution with water alone (Found : C = 68·8; H = 5·0. $C_{26}H_{23}O_5Cl$ requires C = 69·2; H = 5·1%).

5 : 7-*Dimethoxy*-4′-*dimethylamino*-2-*phenyl*-4-*styrylbenzopyrylium chloride* is prepared by gently refluxing an alcoholic solution of 5 : 7-dimethoxy-2-phenyl-4-methylbenzopyrylium chloride and *p*-dimethylaminobenzaldehyde on the water-bath for 15 minutes in absence of hydrogen chloride. A deep blue solution is obtained from which the salt gradually crystallises out during 2 days; it forms glistening, bright green needles from absolute alcohol (m. p. 190°). The alcoholic solution, which is peacock green, changes to deep blue on addition of dilute alkali. On addition of concentrated hydrochloric acid the alcoholic solution becomes orange, due to formation of the styrylbenzopyrylium chloride hydrochloride. Concentrated alkali precipitates a colourless, gelatinous mass which probably consists of the pseudo-base (Found : C = 69·8; H = 6·2. $C_{27}H_{26}O_3NCl,H_2O$ requires C = 69·6; H = 6·0%). The *ferrichloride* separates from acetone in small, green crystals soluble in glacial acetic acid, alcohol, or acetone with a deep purple colour (Found : C = 53·2; H = 4·5; Fe = 9·2. $C_{27}H_{26}O_3NCl_4Fe$ requires C = 53·1; H = 4·3; Fe = 9·2%).

THE UNIVERSITY, LIVERPOOL. [*Received, January 14th*, 1925.]

XCVIII.—*Styrylbenzopyrylium Salts. Part V. Distyryl Derivatives of 7-Hydroxy-2 : 4-dimethylbenzopyrylium Chloride.*

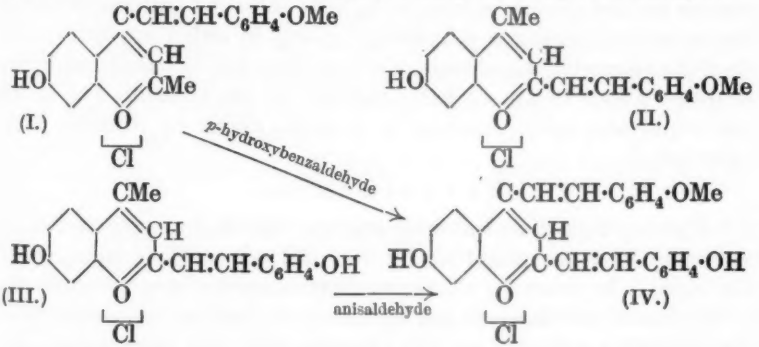
By ISIDOR MORRIS HEILBRON, GEORGE HUGH WALKER, and JOHANNES SYBRANDT BUCK.

THE styrylbenzopyrylium chlorides hitherto prepared (J., 1922, 121, 1198; 1923, 123, 1395, 2521; and preceding paper) have contained only one styryl residue either in the α- or γ-position to the pyrylium oxygen atom. The present communication deals with the preparation of distyrylbenzopyrylium salts containing styryl residues in both the α- and the γ-position, the parent chloride being 7-hydroxy-2 : 4-dimethylbenzopyrylium chloride, $OH\cdot C_6H_3<\begin{matrix}CMe:\\ OCl=CMe\end{matrix}>CH$.

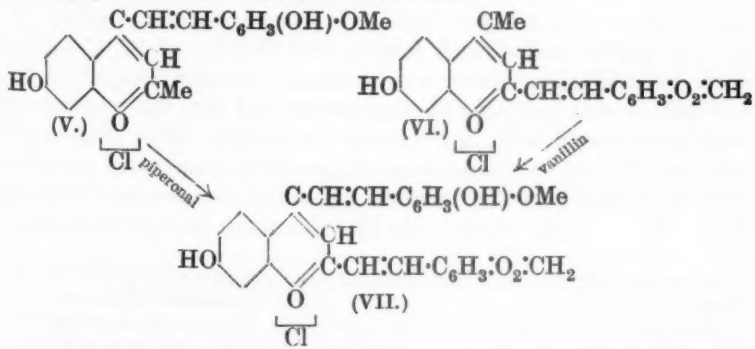
If an aldehyde, A, is condensed with this chloride, and the monostyrylbenzopyrylium derivative obtained further condensed with another aldehyde, B, the resulting distyryl chloride will be different from the one obtained by condensation in the reverse order, provided the aldehyde B in the second case unites with the same methyl group as the aldehyde A in the first case. The comparison of various distyryl chlorides has shown that, in the majority of cases, the pairs of distyryl chlorides containing the same two aldehydes, condensed in the reverse order, have different physical and chemical properties. From this it follows that, although both methyl groups are highly reactive, one must act preferentially in the formation of the monostyryl chloride, which will consequently be a pure compound and not a mixture of α- and γ-derivatives, provided equimolecular quantities of aldehyde and pyrylium chloride are allowed to interact. On the other hand, when two molecules of aldehyde are employed per molecule of the parent chloride, distyrylbenzopyrylium chlorides are formed. In the condensation of anisaldehyde with 7-hydroxy-2 : 4-dimethylbenzopyrylium chloride, two isomeric styrylbenzopyrylium chlorides, a violet and a blue salt, have been isolated by slightly varying the conditions of the reaction. As these give rise to different distyryl derivatives, it is obvious that they represent the α- and γ-monostyryl compounds. Unfortunately, it has proved impossible to fix definitely the configuration of any of these chlorides, and for the purpose of describing them it has been determined to assign to the majority the α-configuration.* That this is in all probability correct may be adduced by collateral evidence drawn

* Borsche and Wunder (*Annalen*, 1916, **411**, 64) assign analogous configurations to the monostyryl chlorides obtained on condensation of the parent chloride with salicylaldehyde, piperonal, and resorcylaldehyde.

from other sources. Thus, in the quinoline series, it has repeatedly been found that the methyl group is more reactive in quinaldine than in lepidine, and Bogert and Nabenhauer have recently shown that the methyl group in 2-methylquinazoline condenses more rapidly with phthalic anhydride than the corresponding group in the 4-position (*J. Amer. Chem. Soc.*, 1924, 46, 1932). The only apparent exceptions among the compounds studied are the blue monoanisyl chloride (I) and the monovanillin chloride, to which the γ-configuration has been assigned. The reason for this is that the former yields with *p*-hydroxybenzaldehyde a distyrylbenzopyrylium chloride (IV) identical with the one isolated by condensing 4′ : 7-dihydroxy-2-styryl-4-methylbenzopyrylium chloride (III) with anisaldehyde, and different from that obtained by condensing the isomeric violet anisyl chloride (II) with *p*-hydroxybenzaldehyde.



Similarly, the monovanillin chloride (V) gives with piperonal a distyryl chloride (VII) identical with the salt obtained by condensation of 7-hydroxy-3′ : 4′-methylenedioxy-2-styryl-4-methylbenzopyrylium chloride (VI) with vanillin.



That the vanillin derivative is abnormal, differing in constitution from the other monostyrylbenzopyrylium salts, is supported by the

fact that it is the only brown monostyryl chloride found in this series.

It is thus clear that these two monostyryl salts are certainly differently constituted from the majority and, on the assumption that the latter are α-derivatives, they must accordingly be representatives of the γ-monostyryl series.

In their properties, both the mono- and the di-styrylbenzopyrylium chlorides closely resemble the salts formerly described. A characteristic feature is the deep green colour of almost all the chlorides containing a *p*-hydroxy-group in the styryl residue. This distinguishes them from the analogous chlorides of the previous series (p. 685), which are usually brown or red with bluish-green reflex. The monostyryl salts dissolve in alcohol with an orange or a red coloration. The distyryl chlorides, on the other hand, form intense reddish-purple solutions in this solvent. All members of this series containing a *p*-hydroxyl group in either styryl residue show the characteristic change of colour from red to blue on addition of dilute alkali to an alcoholic solution of the chloride, but in no case could this colour change be brought about by dilution with water alone.

Experimental.

7-Hydroxy-2 : 4-dimethylbenzopyrylium chloride was prepared from resorcinol and acetylacetone by von Bülow's method (*Ber.*, 1901, **34**, 1189). In order to obtain consistent results in condensations, it was found necessary to purify the crude salt by dissolving it in the minimum quantity of 80% formic acid, and reprecipitate by addition of a mixture of ether and ethyl acetate. Under these conditions it usually forms a bulky, pale yellow product, but if still dark in colour, the above treatment must be repeated.

4′ : 7-Dihydroxy-2-styryl-4-methylbenzopyrylium Chloride * (Formula III).—7-Hydroxy-2 : 4-dimethylbenzopyrylium chloride (7·7 g.) was gently boiled with formic acid (20 c.c. of 80%) until a deep emerald-green colour was produced, allowed to cool to 40°, and mixed with *p*-hydroxybenzaldehyde (4·1 g.), the whole being rapidly saturated with dry hydrogen chloride. After 2 days, the solid was filtered and recrystallised from 90% formic acid saturated with hydrogen chloride, forming glistening, beetle-green crystals, m. p. 260°. If the formic acid contains more than 20% of water,

* Owing to the fact that experimental proof regarding the position of the styryl residue is lacking, the possibility of the alternative configuration as 4′ : 7-dihydroxy-4-styryl-2-methylbenzopyrylium chloride, although less probable on theoretical grounds, cannot be ignored. This applies equally to all other monostyryl and unsymmetrical distyryl salts described in this communication.

the chloride separates in yellowish-green crystals. It is readily soluble in formic acid and glacial acetic acid, sparingly soluble in absolute alcohol with an intense red colour which is changed to deep blue on addition of dilute sodium hydroxide solution [Found : after 1 month over solid KOH, C = 63·5; H = 4·9; Cl (Carius) = 10·1. $C_{18}H_{15}O_3Cl,HCO_2H$ requires C = 63·2; H = 4·7; Cl = 10·0%].

7-Hydroxy-4'-methoxy-2-styryl-4-methylbenzopyrylium chloride (formula II) was similarly prepared. The crude product crystallises from 80% formic acid (deep orange-red solution) in small, purple prisms, m. p. 160°. The orange-red solution in absolute alcohol (*N*/1000 dilution) shows a brown fluorescence, which is immediately destroyed on addition of water.

If, in the preparation of the above chloride, the anisaldehyde is added to the boiling solution, the isomeric salt (formula I) is formed, which crystallises from 80% formic acid in blue-black needles, m. p. 150°. The colours in solution are identical with those of the purple form. As these two varieties lead to different distyrylpyrylium chlorides, it is evident that they are structurally different [Found : (purple form) C = 66·2; H = 5·5; Cl = 10·1. (Blue form) C = 66·1; H = 5·4. $C_{19}H_{17}O_3Cl,H_2O$ requires C = 65·8; H = 5·5; Cl = 10·2%].

4' : 7-Dihydroxy-3'-methoxy-4-styryl-2-methylbenzopyrylium chloride (formula V) crystallises from glacial acetic acid containing 10% of absolute formic acid in small, brown crystals, sparingly soluble in alcohol to a carmine-red solution which becomes blue in presence of dilute alkali (Found : C = 60·8; H = 4·9; Cl = 9·2. $C_{19}H_{17}O_4Cl,H_2CO_2$ requires C = 61·4; H = 4·9; Cl = 9·1%).

3' : 4' : 7-Trihydroxy-2-styryl-4-methylbenzopyrylium chloride is prepared by the direct condensation of protocatechualdehyde with the parent chloride under precisely the same conditions. It separates from the reaction mixture over-night and is recrystallised from absolute formic acid saturated with hydrogen chloride, in which solvent it dissolves with a deep red colour. Green needles having a brilliant golden reflex, only sparingly soluble in glacial acetic acid and in absolute alcohol, the solution in the latter solvent being carmine and changing to deep Prussian blue on addition of alkali (Found : C = 65·1; H = 4·9; Cl = 10·5. $C_{18}H_{15}O_4Cl$ requires C = 65·3; H = 4·5; Cl = 10·7%).

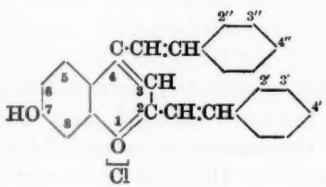
7-Hydroxy-4'-dimethylamino-2-styryl-4-methylbenzopyrylium Chloride.—A solution containing 7-hydroxy-2 : 4-dimethylbenzopyrylium chloride (7 g.) and *p*-dimethylaminobenzaldehyde (5 g.) in absolute alcohol (25 c.c.) was refluxed on a water-bath for 1 hour. Towards the end of the reaction a bronze-violet, crystalline powder was rapidly deposited from the deep blue solution and, after stand-

ing over-night, was filtered. It is only very sparingly soluble in alcohol or glacial acetic acid to a deep blue solution and in formic acid to an olive-green. Owing to its remarkable insolubility, it could not be recrystallised and it was accordingly purified by repeated washing with small quantities of absolute alcohol. Addition of concentrated hydrochloric acid to an alcoholic solution of the chloride gives rise to a yellow solution containing the dichloride (Found : C = 66·5; H = 6·1; Cl = 9·7. $C_{20}H_{20}O_2NCl,H_2O$ requires C = 66·7; H = 6·1; Cl = 9·8%).

4′ : 4″ : 7 - *Trihydroxy* - 2 : 4 - *distyrylbenzopyrylium Chloride*.*—7-Hydroxy-2 : 4-dimethylbenzopyrylium chloride (7·7 g.) and *p*-hydroxybenzaldehyde (8·2 g.) are suspended in hot absolute alcohol (25 c.c.) and a rapid stream of dry hydrogen chloride is passed in during ½ hour, when an intense ruby-red solution is formed. This is set aside and heated occasionally during 5 days, by which time a brilliant, bronze-green powder will have separated. Recrystallised from a mixture of absolute formic acid containing 15% of glacial acetic acid, the salt forms dark green crystals, m. p. 240°, only sparingly soluble in alcohol and acetic acid with reddish-purple coloration. The alcoholic solution changes to Prussian blue on addition of alkali (Found : C = 68·7; H = 5·2; Cl = 7·8. $C_{25}H_{19}O_4Cl,H_2O$ requires C = 68·7; H = 4·8; Cl = 8·1%).

7-*Hydroxy*-4′ : 4″-*dimethoxy*-2 : 4-*distyrylbenzopyrylium chloride* is best prepared by saturating a solution (15 c.c. of alcohol) of the purple monoanisyl chloride (8·2 g.) and anisaldehyde (3·4 g.) with dry hydrogen chloride at room temperature and then refluxing for about an hour. After 12 hours, the blue-green crystalline mass is filtered and kept over cold glacial acetic acid to remove traces of anisaldehyde, which prevent its separation on recrystallisation. It forms greenish-blue prisms from boiling glacial acetic acid, m. p. 170°, and is sparingly soluble in absolute alcohol to a carmine solution with faint brown fluorescence. Addition of alkali changes the colour first to green and then to pale yellow (Found : C = 69·8; H = 5·3; Cl = 7·5. $C_{27}H_{23}O_4Cl,H_2O$ requires C = 69·7; H = 5·4; Cl = 7·6%).

* The positions of the various groups in the distyryl series are numbered as follows :



7-Hydroxy-4'-methoxy-4''-dimethylamino-2 : 4-distyrylbenzopyrylium chloride was prepared by boiling a solution in alcohol (40 c.c.) of the purple monoanisyl salt (10·9 g.) with *p*-dimethylaminobenzaldehyde (4·9 g.) under reflux for ½ hour without the use of hydrogen chloride. The solution rapidly assumed a deep blue colour and, after 12 hours, the separated black powder was filtered, washed with ether, and recrystallised from glacial acetic acid, forming small, black crystals, m. p. 200°, soluble in alcohol to a deep blue solution which changed to purple on addition of a few drops of dilute alkali. In concentrated hydrochloric acid the colour is orange (Found : C = 67·4; H = 5·9; Cl = 7·6. $C_{28}H_{26}O_3NCl,2H_2O$ requires C = 67·8; H = 6·1; Cl = 7·2%).

4' : 7-Dihydroxy-4''-methoxy-2 : 4-distyrylbenzopyrylium Chloride (Formula IV).—4' : 7-Dihydroxy-2-styryl-4-methylbenzopyrylium chloride (13 g.) and anisaldehyde (8·0 g.) were refluxed with absolute alcohol (20 c.c.), saturated with dry hydrogen chloride, for 1½ hours. The somewhat oily mass was washed with alcohol and recrystallised from 80% formic acid saturated with hydrogen chloride, forming dark-brown, shining needles, m. p. 220°, sparingly soluble in glacial acetic acid or alcohol. The solution in the latter solvent is reddish-purple, which changes to deep blue on addition of alkali (Found : C = 68·9; H = 5·2; Cl = 7·9. $C_{26}H_{21}O_4Cl,H_2O$ requires C = 69·2; H = 5·1; Cl = 7·9%).

This chloride is identical with the salt obtained by the condensation of blue monoanisyl chloride (I) with *p*-hydroxybenzaldehyde under precisely similar conditions.

The isomeric 4'' : 7-dihydroxy-4'-methoxy-2 : 4-distyrylbenzopyrylium chloride prepared from the violet monoanisyl chloride and *p*-hydroxybenzaldehyde crystallises from 80% formic acid in dark green crystals, m. p. 160°. The colour in alcohol is identical with that of its isomeride, but on addition of alkali only a dark-green colour is produced, which, however, develops a blue tinge on dilution with water (Found : C = 66·3; H = 5·3. $C_{26}H_{21}O_4Cl,2H_2O$ requires C = 66·5; H = 5·3%).

3' : 4' : 7-Trihydroxy-4''-methoxy-2 : 4-distyrylbenzopyrylium chloride separates from 80% formic acid in emerald-green needles, m. p. 240°, sparingly soluble in alcohol with deep reddish-purple colour (Found : C = 64·6; H = 4·9. $C_{26}H_{21}O_5Cl,2H_2O$ requires C = 64·4; H = 5·2; Cl = 7·3%).

The isomeric *3'' : 4'' : 7-trihydroxy-4'-methoxy-2 : 4-distyrylbenzopyrylium chloride* obtained by the condensation of the violet monoanisyl chloride (II) with protocatechualdehyde forms a dark-green, crystalline powder, m. p. 210°, also containing 2 mols. of H_2O (Found : C = 64·7; H = 5·2; Cl = 7·5 %).

3′ : 4′ : 7-*Trihydroxy*-3″ : 4″-*methylenedioxy*-2 : 4-*distyrylbenzopyrylium Chloride*.—3′ : 4′ : 7-Trihydroxy-2-styryl-4-methylbenzopyrylium chloride (8·2 g.) and piperonal (3·7 g.) in absolute alcohol (15 c.c.) were saturated with dry hydrogen chloride and refluxed for 2 hours. After 12 hours, the separated salt was filtered and recrystallised from 90% formic acid saturated with hydrogen chloride. It forms emerald-green needles with faint golden reflex, m. p. 255°, and is sparingly soluble in glacial acetic acid or alcohol to a deep reddish-purple solution, the colour of the latter becoming pure blue on dilution with water (Found : C = 62·9; H = 4·7. $C_{26}H_{19}O_6Cl,2H_2O$ requires C = 62·6; H = 4·6; Cl = 7·1%).

The isomeric 3″ : 4″ : 7-*trihydroxy*-3′ : 4′-*methylenedioxy*-2 : 4-*distyrylbenzopyrylium chloride*, similarly obtained from 7-hydroxy-3′ : 4′-methylenedioxy-2-styryl-4-methylbenzopyrylium chloride and protocatechualdehyde, forms a dark green, crystalline powder, m. p. 200° (Found : C = 62·2; H = 4·7; Cl = 7·2%).

4″ : 7-*Dihydroxy*-3″-*methoxy*-3′ : 4′-*methylenedioxy*-2 : 4-*distyrylbenzopyrylium chloride* (formula VII) was prepared by the condensation of 7-hydroxy-3′ : 4′-methylenedioxy-2-styryl-4-methylbenzopyrylium chloride (8·5 g.) with vanillin (3·8 g.). The salt crystallises from 80% formic acid as a dark green, crystalline powder, m. p. 180°, and is identical with the salt obtained by condensation of the monostyryl vanillin chloride (V) with piperonal (Found : C = 62·9; H = 5·0; Cl = 6·9. $C_{27}H_{21}O_6Cl,2H_2O$ requires C = 63·2; H = 4·9; Cl = 6·9%).

We desire to thank the Commissioners of the Royal Society and the Council of the Department of Scientific and Industrial Research for a grant to one of us (J. S. B.) in aid of this research.

THE UNIVERSITY, LIVERPOOL. [*Received, January* 14*th*, 1925.]

XCIX.—*A Redetermination of the Atomic Weight of Boron.*

By HENRY VINCENT AIRD BRISCOE and PERCY LUCOCK ROBINSON.

IN 1921, when the work here described was undertaken, the atomic weight of boron, usually taken as 11·0, was evidently uncertain to the extent of one or two units in the first decimal place. Consideration of all the available data for this atomic weight (Briscoe, Robinson, and Stephenson, this vol., p. 150) shows that the values published before 1922 range from B = 11·529 to B = 10·703 and

give in mean approximately B = 10·95. Actually the uncertainty in this mean was even greater than appears from the figures, as it has been shown (*loc. cit.*) that there is reason to regard with grave suspicion all those determinations (14 out of a total of 24) dependent on the weighing of fused borax.

Therefore, in planning this investigation, we resolved to make a preliminary series of analyses to establish the method and then to carry out side by side three distinct and independent series of determinations, using samples of boron from widely separated, known sources, subjecting each sample before analysis to a rigorous purification, and ensuring particularly that all the samples had comparable treatment.

This method of attack was prompted also by another motive: the desire to inquire experimentally whether for boron the isotope-ratio is always and everywhere the same. Hitherto, in the great majority of atomic weight determinations, attention has been wholly concentrated on attaining great purity of the substance taken for analysis and the *origin* of that material has not been considered. Yet in the one case, that of lead, where materials of different known origin have been thoroughly investigated, results of the greatest interest and importance have accrued. These investigations, of course, arose from, and served to confirm, speculations as to the radio-active origin of lead, but it seems possible that an equally exhaustive examination of specimens of some of the lighter elements from different sources might throw some light upon the problem, at present quite obscure, of the origin and history of the elements in general. Several atomic weight determinations for elements other than boron, referred to in more detail later and published during the progress of this research, have evidently been undertaken with this possibility in view: but it seems desirable to state it clearly here as a primary reason for our work.

The choice of a ratio for measurement was made only after a careful review of all the known compounds of boron. Excluding borax, for the reason already given, there remain few compounds at all likely to be obtainable pure and of constant and definite composition. Among these boron trisulphide and the additive compound of boron trifluoride and ammonia seem promising, but they have been little investigated and involve methods of analysis either difficult and untried or obviously unsuited to precise work. Boron trichloride and tribromide are definite and stable compounds, the properties of which are well-known: although extremely sensitive to moisture, they appear to be the compounds best suited to

precise analysis. Therefore it was decided to determine in this case the ratio $BCl_3 : 3Ag$.

Preliminary tests made by adding to a litre of pure water 1·5 g. of boric acid and 2·5 g. of silver nitrate gave a perfectly clear solution whether nitric acid (12·0 c.c. of concentrated acid) were added or not, and thus showed that silver borate is not precipitated under the conditions obtaining in the titration of a chloride with silver in presence of nitric acid by the usual procedure. Therefore the method of analysis adopted consisted in weighing boron trichloride in sealed glass bulbs, breaking the bulbs in water, and titrating the hydrochloric acid in the resulting dilute solution of boric and hydrochloric acids with silver nitrate prepared from a weighed amount of pure silver, the end-point being ascertained nephelometrically.

Weighing.

Throughout this work the special Oertling balance with the separately enclosed steel beam and the set of weights described in a previous communication (Robinson and Briscoe, this vol., p. 138) were used. The balance was kept in a darkened room having a north aspect and was illuminated by artificial light falling normally on the front of the balance. Both the zero and the sensitivity, the latter set at about 33 scale divisions per milligram, remained very constant throughout. As the inequality of the arms was very small and constant for all loads and as relative weights only were desired, all weighings and calibrations were made directly and not by reversal or substitution.

In weighing out metallic silver, etched buttons of nearly the desired weight, with pieces of pure silver wire and foil as make up, were weighed out (a valuable check) on a standard No. 7 S. W. Oertling balance, dried for 12 hours at 250° in an electrically heated glass oven, cooled beside the balance in a desiccator over solid caustic potash, transferred to the balance pan, and weighed within ½ hour. Vacuum weights of silver were ascertained by applying to the apparent weight a correction determined by the density of silver (10·49) and the density of air at the pressure and temperature observed during weighing.

The weights of boron trichloride were ascertained in the manner previously described in detail with illustrative data (Briscoe and Little, J., 1914, **105**, 1330; Briscoe, J., 1915, **107**, 72). Bulbs and stems filled with dry air were each weighed on three separate occasions against a tare, the temperature and barometric pressure being noted at the time of each weighing. After being filled and sealed off from the stem, bulbs and stems were again weighed on two separate occasions against the same tare. Then the external

volume of each bulb was determined by weighing in air and in water and, the density (as the mean of concordant determinations on four samples) and actual weight of the glass of the bulb being known, the internal volume of the bulb, and hence the weight of air originally contained in the bulb was calculated. The relative vacuum weight of the boron trichloride in the bulb is evidently the apparent weight (increase in excess weight over tare) *plus* this weight of air. Before each weighing the bulbs and stems and tares were carefully wiped with well-washed pure linen and then allowed to stand in the balance case for 8—12 hours.

This method of weighing sensitive materials is evidently less well known than it should be. Weatherill (*J. Amer. Chem. Soc.*, 1924, **46**, 2442) has recently confirmed that its error is probably no greater than the error of weighing, 0·01—0·02 mg., but is apparently unaware of the prior description and use of the method by one of us, as the procedure in experiment and calculation is again described in detail and no reference is made to the prior publication.

The weights and gold half-milligram rider were repeatedly calibrated to ascertain their relative weights in air, and were always used on the same (right hand) balance pan: in all weighings, a correction was applied for the calibration error.

The error in weighing was less than 0·02 mg. and weights of boron trichloride are stated to the nearest 0·01 mg. Weights of silver are stated in the same manner, but are affected by the possible error in the nephelometric determination of the end-point, approximately 0·00005 g.

It has been stated (Manley, *Phil. Trans.*, 1913, **212**, [*A*], 227) that objects dried in an enclosed space alongside solid caustic potash can become contaminated with alkali. As this drying agent was extensively used in this and earlier determinations, the experiments described below were made to ascertain whether such contamination occurs under the conditions of the normal use of this drying agent.

As a test for alkali a solution of phenolphthalein, made very faintly pink with alkali, was used: one drop of it added to 0·05 c.c. of *N*/100-caustic soda (0·00002 g.) in 10 c.c. of water gave a distinct red coloration.

1. During more than 2 years the upper and lower compartments of the balance case had been dried by means of vessels containing caustic potash stood close against the back of the case and renewed from time to time, as the alkali deliquesced. Therefore the back pane of glass was removed from the case, flooded with about 5 c.c. of water, and the washings were tested with phenolphthalein. No trace of alkali could be detected.

2. A fairly rapid current of air saturated with water vapour was passed first through a 50% solution of caustic potash, secondly through a tower packed with solid caustic potash, and then on to the surface of about 10 c.c. of phenolphthalein solution placed in a clean wash-bottle, which had been used for distilled water for 5 years. This experiment was run continuously for 500 hours, but no trace of red coloration developed.

Therefore it is clear that caustic potash does not contaminate an air stream passed over it or glass surfaces in its neighbourhood.

Purification of Reagents.

The methods adopted for the purification of all the accessory reagents and of the main supply of silver have been sufficiently described (Robinson and Briscoe, *loc. cit.*). It is here only necessary to add that the small pieces of silver used to adjust the weights of the silver buttons were in part pieces of wire of various gauges remaining from a previous investigation (Briscoe, *loc. cit.*) and in part pieces cut from thin sheet silver with clean steel scissors, etched with nitric acid, well washed, and dried at 250°. The sheet silver was prepared by hammering and then rolling a large button of pure silver between sheets of parchment.

Three samples of silver were used, namely, Silver I, Silver A, and Silver B. The preparation of the materials A and B has been previously described (Robinson and Briscoe, *loc. cit.*). Silver I, used only in the preliminary work, was metal prepared from silver nitrate by the Stas bisulphite method and subsequently dissolved in nitric acid and reprecipitated in the same way. There is every reason to believe that the samples of silver were uniform and that A and B were closely similar : results obtained with them should, therefore, be strictly comparable. Any constant impurity in the silver would, of course, affect the absolute value of the results, but numerous investigations have shown that the method employed for preparing the silver yields a product containing but 1 part of impurity in 300,000 parts, the effect of which on the results is negligible in comparison with that of other sources of error.

Preparation and Purification of Boron Trichloride.

Sources.—The boron trichloride used in the preliminary series of analyses (sample i) was prepared from boric acid of unknown origin in stock in the laboratory. That used for the three main series was prepared from the following materials :

Sample (ii) Crude boric acid from the neighbourhood of Volterra, Tuscany.

Sample (iii) Boracite from Sultan Tchair, Asia Minor.

Sample (iv) Colemanite (calcined) from Death Valley, California, U.S.A.

We are indebted to Messrs. Borax Consolidated, Ltd., for supplies of these minerals and for detailed information as to their origin, and would here express our thanks to Mr. R. C. Baker, managing director of that company, for his personal interest in securing for us this essential starting material.

Preparation of Boric Acid.—Sample (i) was used without purification: sample (ii) was recrystallised once from a filtered solution in dilute hydrochloric acid. The boracite ($6MgO,MgCl_2,8B_2O_3$) sample (iii) and colemanite ($Ca_2B_6O_{11},xH_2O$) sample (iv) were each dissolved in boiling 1 : 1 hydrochloric acid, and the solution was diluted with its own bulk of boiling water, filtered at the boiling point in a jacketed funnel, and cooled to obtain a crop of white, crystalline boric acid, which was filtered off and dried.

Preparation of Boron Trichloride.—Dumas's method (*Ann. Chim. Phys.*, 1826, [ii], **31**, 436) was tried by heating in chlorine (*a*) a mixture of ground boric oxide glass and carbon, and (*b*) charcoal soaked in hot concentrated boric acid solution, and dried; and also by striking an arc between a carbon rod and mixture (*a*) in an atmosphere of chlorine. The heating of boron nitride in chlorine and of boric oxide glass in carbon tetrachloride vapour were also investigated, but none of these methods gave a yield of boron trichloride sufficient to warrant its adoption. The heating of boric acid with phosphorus pentachloride (Gustavson, *Ber.*, 1870, **3**, 426; 1871, **4**, 975) seemed so likely to introduce volatile phosphorus chlorides as an impurity that it was not attempted. Thus it became necessary to adopt the wasteful and troublesome process of preparing and chlorinating elementary boron.

Anhydrous boric oxide was obtained by gradually feeding boric acid into a clay crucible kept at a bright red heat until the crucible was three-quarters filled, and keeping the melt at 1000°, until all evolution of steam had ceased. The resulting glass was poured on to a cold iron plate, crushed, and then ground in a Weatherhead crusher to pass a sieve of 50 meshes to the linear inch.

This oxide was then reduced with magnesium, according to the method usually attributed to Moissan, although it had been used by earlier workers (Phipson, *Proc. Roy. Soc.*, 1864, **13**, 217; Jones, J., 1879, **34**, 42; Winkler, *Ber.*, 1890, **23**, 772: see also Moissan, *Compt. rend.*, 1892, **114**, 319; Weintraub, *Trans. Amer. Electrochem. Soc.*, 1909, **16**, 165; Ray, J., 1914, **105**, 2162). A mixture of 70 parts of powdered boric anhydride with 50 parts of magnesium powder contained in a clay crucible and covered with a 2-inch layer of powdered charcoal was heated in a furnace until reaction

took place. Then the air supply to the furnace was immediately cut off and the crucible and its contents were allowed to cool in a reducing atmosphere. This procedure served greatly to minimise the serious loss of boron by reoxidation, found to occur when the porous mass produced by the reaction was exposed to air whilst hot. Working details of the successful method are given, as failure attended attempts to conduct the reaction in closed vessels in an atmosphere of hydrogen and by other methods. The furnace used in all this work, a 20 lb. " Captive Fire " furnace, fired with a correct mixture of coal-gas and air, both supplied under pressure, proved specially convenient for the operations described. The coke-like product, freed from admixed lumps of charcoal, was powdered, digested for 24 hours with concentrated hydrochloric acid to decompose borides and dissolve metallic oxides present, and boiled with an equal bulk of water. After settling, the clear liquor was decanted, the residue was again twice extracted with boiling dilute hydrochloric acid and was then filtered off, washed, and dried at 100°. Some difficulty was encountered in converting this boron to the trichloride. At first, it was heated in a current of chlorine in a silica tube wound with nichrome wire and heated electrically, but it was soon found that, even at a dull red heat, the boron trichloride rapidly attacked the silica, one tube being perforated in a few hours, and the product contained considerable quantities of silicon tetrachloride. An attempt to protect the silica from attack by flooding the inner surface with concentrated magnesium nitrate solution and igniting this to oxide, thus brasquing the tube with magnesia, proved useless. An alundum tube was even more seriously attacked and was speedily blocked up by volatilised aluminium chloride : it also proved so porous as to permit a serious amount of chlorine to leak into the atmosphere : hence its use was abandoned. Ultimately, it was found that a tube of hard Jena glass, heated at about 450—500° only, by slipping over it a wider silica tube heated electrically, was scarcely attacked, could be washed out and re-used repeatedly, and gave a product almost free from silicon chloride.

Gas from a cylinder of liquid chlorine passed through a pressure gauge and safety valve consisting of a T-tube dipping into a tall jar of concentrated sulphuric acid, and then through a Drechsel bottle containing the same acid, into the reaction tube. This tube, about 36 inches long and $\frac{3}{4}$ inch in diameter, was fitted at one end with a waxed cork carrying the leading tube for chlorine : at the other end a glass adapter, attached by wide rubber tubing, led the products into a glass receiving vessel, of the form shown in Fig. 3 (R_1, R_2, etc.), cooled with solid carbon dioxide. This refrigerant

was used because it was found that ordinary freezing mixtures allowed some chlorine (b. p. −33°) to pass and this carried away a considerable proportion of the boron trichloride (b. p. +12·5°). At the end of each run both tubes of the receiver were drawn down to capillaries (to permit reopening) and sealed before the blowpipe.

Another serious trouble in the earlier chlorinations was the frequent stoppage of the tubes with a white solid, which proved to be boric anhydride. Though, as others have noted (see, *e.g.*, Stock and Holle, *Ber.*, 1908, **41**, 2095), the boron was undoubtedly impure, the proportion of oxide it contained was quite insufficient to account for the quantity found in the tubes. Therefore it seemed probable that the trouble must be due to water persistently retained by the boron powder, and it was found that if this boron, immediately before chlorination, was dried by heating to redness in a silica tube in a current of dry hydrogen, the deposition of boric anhydride was so far minimised as to make the process workable : this procedure was therefore adopted throughout the preparations of boron trichloride.

Purification of Boron Trichloride.—The crude material contained considerable amounts of chlorine, hydrogen chloride, boric oxide, ferric chloride, and insoluble matters, and owing to the thoroughly unsatisfactory nature of the method of preparation many other impurities may have been present, including such volatile chlorides as chloroform, carbon tetrachloride, phosphorus trichloride, silicon tetrachloride, etc. Therefore, it was necessary to adopt a very elaborate process of purification, and as, evidently, the value of the determination wholly depends on the efficiency of this process, it must be described in detail.

The purification of sample (i) for the preliminary series was, of course, experimental and its actual treatment is sufficiently shown in Fig. 1. All the main series samples (ii), (iii), and (iv) received substantially identical treatment comprising the following stages :

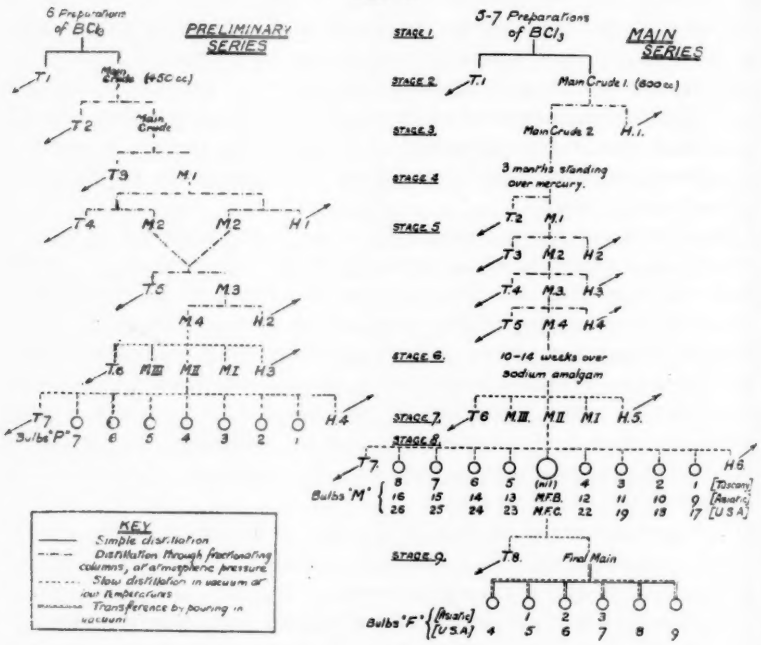
1. Distillation from various receivers into a large bulb.
2. Distillation into the single-column fractionating still.
3. Distillation in this still, with thorough fractionation, whereby chlorine and hydrogen chloride were almost completely removed.
4. Standing and frequent shaking in a sealed bulb with mercury for 3 months or longer.
5. Systematic fractional distillation in three stages, conducted in dry air at about atmospheric pressure in the " three-column still."
6. Standing and frequent shaking in a sealed bulb with sodium amalgam for about 3 months.
7. Fractional distillation into five fractions in a vacuum.

8. Fractional distillation of the middle fraction in a vacuum, and collection in bulbs.

9. In the case of samples (iii) and (iv) a middle fraction, collected among the bulbs for analysis, was further redistilled, leaving a residual fraction, and the distillate transferred to weighed bulbs by pouring.

This typical scheme of purification for the main samples is shown diagrammatically in Fig. 1. With regard to the treatment of individual samples it is only necessary to remark that the treatment

FIG. 1.

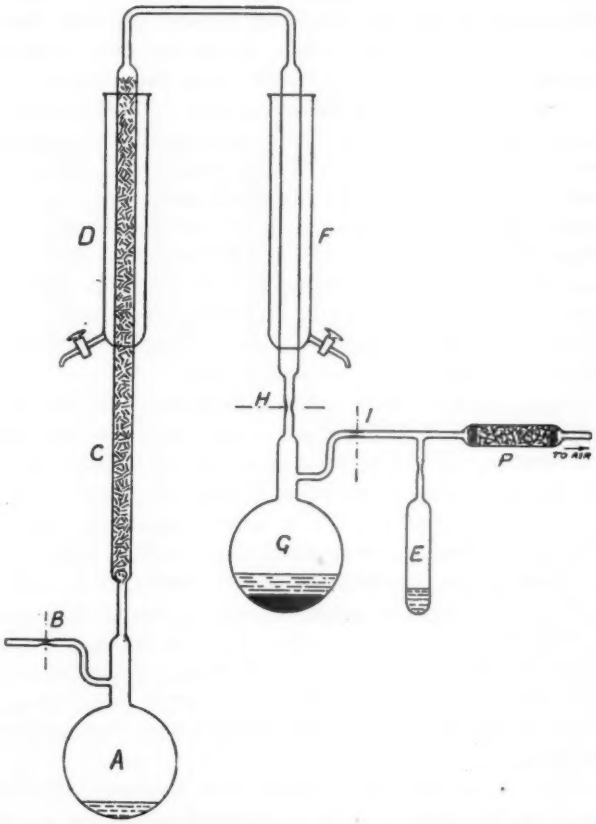


of sample (ii) differed from that of (iii) and (iv) in the following details : (*a*) stage 5 comprised two separate handlings in a "two-column still" instead of one in the "three-column still" described below : (*b*) After the sample had been sealed up at the end of stage 5, it was found that the sodium amalgam had been omitted from the bulb. Fortunately, as the bulb had a "special joint," this could be rectified by transferring the contents to another similar bulb containing sodium amalgam : an attempt to effect this by distillation failed owing to the receiver becoming air-locked, but by freezing the amalgam solid in the bottom of the receiver with liquid air, it became possible to invert the apparatus and

transfer the boron trichloride by pouring, and this was successfully accomplished; (*c*) the quantity of material in the final main fraction of stage 6 was little more than sufficient to fill eight bulbs and yielded a middle fraction (marked "nil," Fig. 1) too small to carry to stage 9.

The apparatus employed may be understood by reference to the "one-column" and "three-column" stills used for stages 3 and 5

FIG. 2.



of the main series purification (Fig. 1) shown in Figs. 2 and 3. The columns C were 2 cm. in diameter and 60 cm. in packed length, filled with hollow cylindrical glass beads 4 mm. in diameter and 4 mm. long (Raschig, Eng. Pat. 1914, No. 6288), supported by a perforated bulb at the bottom. The upper half of each was surrounded by a glass jacket containing water kept at 10° by stirring in crushed ice, and acted as a regulated temperature still-head.

That such columns are very efficient (see, *e.g.*, Lessing, *J. Soc. Chem. Ind.*, 1920, **40**, 115T) was confirmed by the fact that, during the first distillation, a sharp demarcation between the deep yellow chlorine and colourless boron trichloride occurred within 2 cm. in the column and moved steadily up as the last of the chlorine was removed.

In using the "one-column still" (Fig. 2), the apparatus was filled with dry air, and then crude boron trichloride, previously collected into one vessel by distillation from the several receivers, was distilled into A *via* the side-tube, B, and this was then sealed off at the constriction. The jacket, D, having been cooled to 10°, A was immersed in water at 15—20° until the chlorine had been distilled off and swept out of the apparatus. Then, F and G being kept warm enough to prevent any condensation, a considerable head fraction was distilled into E and sealed off. Finally, F was cooled with ice and G with solid carbon dioxide, and a main fraction was distilled into G, which was then sealed off at H and I, leaving a considerable tail fraction in A. During the distillation the apparatus was open to the atmosphere through an efficient phosphorus pentoxide tube, P. In G, the boron trichloride stood, and was frequently shaken, during about 3 months in contact with pure mercury previously placed in the bulb.

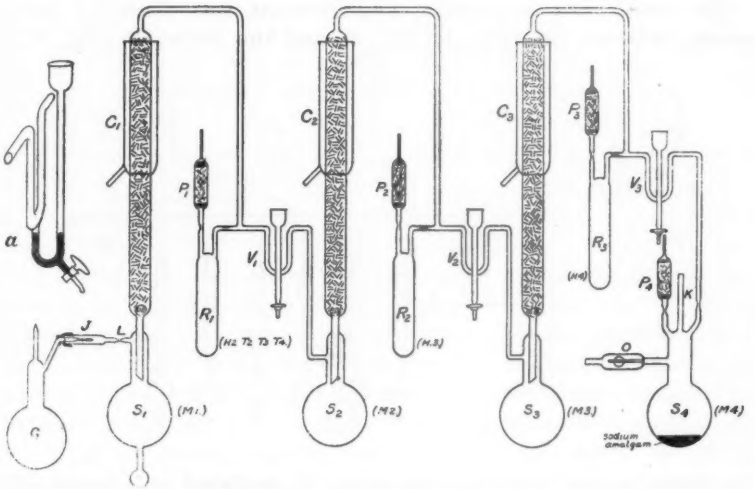
The "three-column still," shown diagrammatically in Fig. 3, consisted of four bulbs, S, of 800 c.c. capacity, the first three each having a column, C, leading to a receiver, R, open to air through a phosphorus pentoxide guard tube, P, and connected *via* a mercury valve, V, to the next bulb. The whole apparatus was clamped around a single large retort-stand and sealed together. From Fig. 3a, showing the construction of the valves, it is evident how, by lowering or raising the mercury level in the U-tube, connexion between the two sides of the valve may be made or broken, and thus how it is possible to direct vapour into any desired part of the apparatus and conduct a systematic fractional distillation without bringing the boron trichloride into contact with any material other than dry glass, mercury, and air.

The valves V having been sealed with mercury, the apparatus was first dried by passing in at J a current of dry air and allowing it to pass away first through P_1, and then successively through P_2, P_3, and P_4, the capillary exit tubes being sealed or cut open as required. During this operation all parts of the apparatus in turn were repeatedly heated to 150—200°. Then a quantity of pure sodium amalgam was filtered into S_4 through the tube K, and this tube was sealed off. The current of dry air was now reversed, passing in at P_4 and out at J, and the bulb, G, containing mercury

and a main fraction of crude boron trichloride from the previous distillation, was connected at J by a glass-and-rubber joint flexible enough to allow the sealed capillary of G to be broken within it. Then M 1 was cooled, the lower part in ice and the neck by a collar of solid carbon dioxide, and G was warmed at 15° until the liquid had distilled over, leaving a small tail fraction in G, which was finally sealed off at L.

The material was now completely protected against moisture, and the distillations constituting stage 5 (Fig. 1) were carried out in a manner which is obvious from Fig. 3 and the preceding description.

FIG. 3.



Rejected head and tail fractions were collected in the bulbs R, which were sealed off, immediately they had received the fractions shown (in brackets) against them, in the order R_2, R_3, R_1. The final main fraction, M 4, was collected and sealed up with the sodium amalgam in bulb S_4, provided with a "special joint," O: it stood in the bulb, and was frequently shaken, during 10—14 weeks.

During the last distillation of this stage readings of a thermometer enclosed in the upper part of column C_3 gave readings for the boiling point of boron trichloride which, when corrected for the observed atmospheric pressure at the time of distillation, agreed closely with the value 12·5° found by Stock and Priess (*Ber.*, 1914, **47**, 3109).

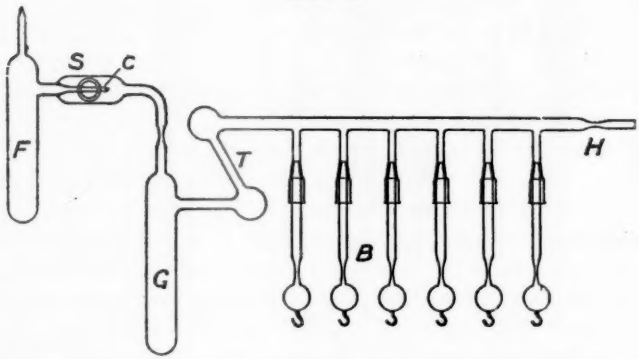
The remaining stages of the purification and the transference into bulbs were carried out in a vacuum by a method essentially

similar to that first described by one of us (Briscoe and Little, *loc. cit.*), and since used in several other precise investigations (see, *e.g.*, Brauner and Krepelka, *J. Amer. Chem. Soc.*, 1920, **42**, 1917; Krepelka, *ibid.*, p. 925; Baxter, Weatherill, and Holmes, *ibid.*, p. 1194; Baxter, Weatherill, and Scripture, *Proc. Amer. Acad. Arts Sci.*, 1923, **58**, 245).

The " special joint " which makes this method possible was used by one of us in the purification of vanadyl trichloride early in 1912, and was described as new in 1914, but it has recently come to our knowledge that the use of a closely similar device, though for another purpose, was described (Bruner and Bekier, *Z. Elektrochem.*, 1912, **18**, 369) prior to our publication.

One small, but important, improvement was made by interposing between the special joint, S, and the bulbs, B (Fig. 4), a

FIG. 4.



two-bulb trap of the form shown at T, designed to prevent any fragments of broken glass being carried over into the bulbs by the stream of vapour when the capillary C is broken. Weatherill (*loc. cit.*) also has found this precaution desirable.

In two cases the quantity of boron trichloride in the main fraction was more than enough to fill eight bulbs, and the excess was collected as a middle fraction in a separate bulb, F (Fig. 4), and subsequently transferred to weighed bulbs in the following way.

The bulb F was fused on to the remainder of the system shown in Fig. 4 and then was heated, repeatedly evacuated, and finally sealed off at H. The special joint K was then opened, and the liquid was distilled into G, leaving a last fraction in F, which was then sealed off. The whole apparatus was next inverted and the liquid transferred to the bulbs by pouring, assisted by alternate heating and cooling of the bulbs, in alcohol at $-20°$ and in liquid air respectively.

This operation was performed with the material for the Final Series B and C: in both cases the tail fraction in F was carefully distilled into the side tube and left no trace of visible residue.

Tests of the Efficiency of the Method of Purification.

This is evidently a case in which the efficiency of the scheme of purification is exceptionally important and every attempt was made to secure direct experimental evidence on this point. The effect of the possible impurities upon the atomic weight is shown in Table I, whence it is evident that the elimination of boric oxide, chlorine, and hydrogen chloride is specially important.

TABLE I.

Impurity.	Change in the atomic weight of boron produced by the presence of 0·1% of the impurity in BCl_3.	B. p.
Boron trioxide, B_2O_3	+0·108	—
Chlorine, Cl_2	−0·012	−33·6°
Hydrogen chloride, HCl	−0·008	−83·1
Silicon tetrachloride, $SiCl_4$	+0·009	+59·6
Phosphorus trichloride, PCl_3	+0·017	+76
Arsenic trichloride, $AsCl_3$	+0·042	+130·2
Antimony trichloride, $SbCl_3$	+0·046	+223·5

By a fortunate chance, at a later stage of the purification of the material for the Preliminary Series, a phenomenon was observed which has, apparently, escaped the notice of other workers using boron trichloride. From mere curiosity, the residual fractions from some of the less pure samples of boron trichloride were distilled to dryness: they left a colourless, non-crystalline, and apparently gelatinous or syrupy residue which, when warmed to 40—50°, intumesced and left a white, amorphous solid. On standing in boron trichloride vapour, the solid first became translucent and then deliquesced to a liquid: it was evidently volatile with boron trichloride and probably consisted wholly or largely of boric acid or boric oxide. It was investigated by the following experiments, making use of fractions from the distillations of the Preliminary Series, transferred in a vacuum by means of special joints in the usual way.

A quantity of pure boron trichloride, leaving on evaporation practically no trace of residue, was distilled (*a*) partly on to powdered boric oxide glass, dried at 300° in a vacuum, and (*b*) partly on to boric acid dried at 100° in a vacuum. In both cases the solid dissolved and the solution yielded a distillate that left on evaporation a large, gummy residue, showing precisely the behaviour described above. Thus it was proved that boric acid and boric oxide are volatile in boron trichloride.

In order to ascertain whether this residue could be separated by distillation, a bulb, A, containing about 30 g. of boron trichloride (T 6 of the Preliminary Series) was connected by its special joint to a second evacuated bulb, B. When the liquid was distilled into B, a small but distinct residue was left in A : when the distillate in B was completely redistilled back into A, a much smaller, but still distinctly visible patch of residue remained in B. Then about one-quarter of the liquid in A was repeatedly distilled into B and *poured* back into A until no trace of residue remained on warming B. Finally, about two-thirds of the liquid was distilled into B and then redistilled back into A, when but a very small trace of residue remained in B. These observations prove that the residue can be progressively diminished by fractional distillation in a vacuum, and render it probable that it can thus be eliminated.

It is well established that mercury reacts with anhydrous chlorine : hence the prolonged treatment given in this case (until a clean surface of the metal remained bright indefinitely) should have ensured the removal of all free halogen. There exists no such evidence that anhydrous hydrogen chloride reacts with sodium amalgam, therefore a sealed bulb containing about 100 g. of clean 2% sodium amalgam and a sealed thin capillary tube containing about 0·15 g. of water were placed in a stout cylindrical bulb sealed to a closed-end mercury pressure gauge, and about 40 g. of good boron trichloride were distilled into and sealed up in the bulb. The bulb and capillary containing the amalgam and water were broken by vigorous shaking and the apparatus was set up in a room having a fairly constant temperature and kept under observation for several weeks.

There was a steady evolution of gas and rise of pressure, and this continued at a diminishing rate for more than 14 days, affording clear evidence that hydrogen chloride does react with sodium amalgam under the anhydrous conditions obtaining in the process of purification.

A separate experiment showed that pure boron trichloride had no action on sodium amalgam.

The removal of impurities was also followed analytically : about 6 c.c. of boron trichloride were decomposed with water, the solution was divided into equal parts, and these were treated (*a*) with nitric acid and (*b*) with nitric acid and ammonium molybdate, warmed, and allowed to stand several days. Several of the earlier tail fractions gave (*a*) a distinct gelatinous precipitate, probably silica, and (*b*) a slight yellow precipitate of ammonium phosphomolybdate : the later tail fractions gave no evidence whatever of silica or phosphoric acid.

Method of Analysis.

In previous determinations of the ratio of boron trichloride to silver, the bulbs have usually been broken in dilute pure ammonia. The presence of excess of ammonia, obviously desirable as a precaution against loss of hydrogen chloride if the solution has to be filtered from the fragments of the bulb, was clearly unnecessary in this case, as all the weighings requisite to determine the vacuum weight of boron trichloride had been made before the analysis was begun.

In each titration the bulb containing boron trichloride, suspended by its hook from a hooked glass rod, was washed and then lowered into about 2000 c.c. of pure water contained in a thoroughly clean resistance glass bottle of 4000—6000 c.c. capacity. The bottle was closed with its carefully fitted and polished stopper, cooled in ice for an hour to reduce the internal pressure, and then vigorously shaken to break the bulb. The reaction between boron trichloride and water was quickly over and produced a perfectly clear and colourless solution, but left some fog in the bottle: therefore the bottle was well shaken at frequent intervals until the fog had completely disappeared and then allowed to stand for at least 3 hours before it was opened.

Meanwhile a quantity of pure silver, calculated to be within a few tenths of a milligram of that required, having been accurately weighed, was dissolved in pure aqueous nitric acid (1 : 1) in a Jena glass solution flask of the special form previously described (Briscoe, J., 1915, **107**, 78), and the solution was heated to boiling, to expel nitrous fumes, cooled, and diluted to about 1200 c.c.

The stopper was carefully removed from the titration bottle and rinsed, the fragments of the glass bulb, especially the capillary ends, were broken up by means of a long, stout glass rod, and the silver solution and rinsings were transferred to the bottle *via* the side tube in the manner described in detail elsewhere.

This transference and all subsequent operations were carried out in orange light in a darkened laboratory set aside solely for these titrations and kept free from all possible sources of contamination with chlorine or silver.

The solution was gently swirled during the addition of silver and immediately thereafter the bottle was stoppered, vigorously shaken at frequent intervals during 2—3 hours, allowed to stand at room temperature for 7—10 days, being well shaken twice or thrice each day, and then packed in ice for about 48 hours.

Then 100 c.c. of the clear supernatant liquid were withdrawn with a pipette and used for duplicate nephelometric tests in the

Table II.

Data and Results of Analyses.

Number of analysis.	Sample of silver.	Relative vacuum wt. (g.) of BCl_3.	Relative vacuum wt. (g.) of silver.	Ratio : $BCl_3/3Ag$.	Atomic wt. of boron (Ag = 107·880; Cl = 35·457).	Individual and average deviations from mean.
		Preliminary Series.				
P 1	Silver 1	7·10616	19·61748	0·362236	10·854	+0·002
P 2						
P 3	„ 1	8·06893	22·28012	0·362158	10·829	−0·023
P 4	„ 1	9·91393	27·37313	0·362177	10·835	−0·017
P 5						
P 6	„ 1	7·42801	20·49990	0·362344	10·889	+0·037
				Means	10·852	±0·020
		Main Series.				
		A. Boron from Boric Acid, Volterra, Tuscany.				
M 1						
M 2	Silver A	7·73567	21·35379	0·362262	10·862	+0·022
M 3	„ B	9·83151	27·14230	0·362221	10·849	+0·009
M 4	„ A	7·88427	21·76764	0·362201	10·843	+0·003
M 5	„ A	6·61346	18·26253	0·362133	10·821	−0·019
M 6						
M 7	„ A	7·51389	20·74865	0·362139	10·823	−0·017
M 8				Means	10·840	±0·014
		B. Boron from Boracite, Sultan Tchair, Asia Minor.				
M 9						
M 10	Silver A	7·88217	21·76472	0·362153	10·827	+0·008
M 11	„ B	7·00794	19·35154	0·362139	10·823	+0·004
M 12	„ A	11·56846	31·94600	0·362126	10·818	−0·001
M.F.B.						
M 13	„ A	12·04670	33·26752	0·362116	10·815	−0·004
M 14	„ B	11·39071	31·45640	0·362111	10·814	−0·005
M 15	„ A	8·45278	23·34215	0·362125	10·818	−0·001
M 16				Means	10·819	±0·004
		C. Boron from Colemanite, Death Valley, California, U.S.A.				
M 17						
M 18	Silver A	9·93543	27·42992	0·362212	10·846	−0·009
M 19*	„ B	6·69247	18·47861	0·362174	10·834	−0·021
M 22	„ A	6·87297	18·97723	0·362169	10·832	−0·023
M.F.C.						
M 23	„ A	8·66792	23·92939	0·362229	10·852	−0·003
M 24	„ B	8·08918	22·32812	0·362287	10·870	+0·015
M 25	„ A	5·95008	16·42010	0·362366	10·896	+0·041
M 26				Means	10·855	±0·019
		Final Series B (from fraction M.F.B.. Main Series B).				
F 1	Silver B	5·96256	16·46538	0·362127	10·819	+0·001
F 2	„ B	5·83978	16·12666	0·362120	10·816	−0·002
F 3	„ B	5·31851	14·68670	0·362131	10·820	+0·002
				Means	10·818	±0·002
		Final Series C (from fraction M.F.C., Main Series C).				
F 4	Silver B	2·94096	8·11982	0·362195	10·841	+0·001
F 5	„ A	4·86840	13·44182	0·362184	10·837	−0·003
F 6	„ A	4·89699	13·52005	0·362202	10·843	+0·003
F 7	„ A	5·72597	15·80980	0·362179	10·836	−0·004
F 8	„ A	9·24458	25·52406	0·362190	10·839	−0·001
F 9	„ B	4·69097	12·95092	0·362211	10·846	+0·006
				Means	10·840	±0·003

* Bulbs M 20 and M 21 were tares.

usual manner (Briscoe and Little, J., 1914, **105**, 1322). After an appropriate addition of silver or chloride had been made, in the form of a solution containing 0·0002 g. of silver or its equivalent per c.c., the bottle was again stoppered, shaken, and repacked in ice for 48 hours before another nephelometric test was made. When two such tests separated by 6—7 days agreed in showing that the equivalent concentrations of silver and chloride in the solutions differed by less than 2%, the titration was regarded as finished.

Statement and Discussion of Results.

Table II states the data and results for the Preliminary Series, the three Main Series, and the two Final Series. In order to examine their significance, it is important to understand the relationship of the fractions with which they were obtained; therefore the names of the fractions not analysed are included in each group, the fractions are given in order of separation, *i.e.*, in the Preliminary and the Main Series the most volatile fractions first in each group, and the results are summarised in Table III.

TABLE III.

Summary of Results.

α = *Number of Fraction*; β = *Atomic Weight of Boron* (*deduced*).

	Main Series A.								
α	M 1.	M 2.	M 3.	M 4.	M.F.A. ("nil")	M 5.	M 6.	M 7.	M 8.
β	—	10·862	10·849	10·843	—	10·821	—	10·823	—
	Main Series B.								
α	M 9.	M 10.	M 11.	M 12.	M.F.B.	M 13.	M 14.	M 15.	M 16.
β	—	10·827	10·823	10·818	—	10·815	10·814	10·818	—
	Main Series C.								
α	M 17.	M 18.	M 19.	M 22.	M.F.C.	M 23.	M 24.	M 25.	M 26.
β	—	10·846	10·834	10·832	—	10·852	10·870	10·897	—

	Final Series B.		
α	F 1.	F 2.	F 3.
β	10·819	10·816	10·820

	Final Series C.					
α	F 4.	F 5.	F 6.	F 7.	F 8.	F 9.
β	10·841	10·837	10·843	10·836	10·839	10·846

The analysis of fraction M 6 was lost through an accident, but with this exception every analysis begun was completed and is recorded in the table. Both in the final transference to bulbs and in the analyses, the Series were dealt with in the order in which they are there named: the order of the analyses within each series was irregular and is immaterial.

The Preliminary Series, made with boron trichloride of unknown origin, was carried out simply to gain experience, and the variation

in the results was at first supposed to have no significance, especially as the series contained but six bulbs and the *end* fractions were analysed. As the results for the Main Series A, B, and C accumulated, it was apparent that they exhibited a variation of similar type and it at once became important to ascertain whether this variation was accidental and due to errors in the analyses, or arose from a real change in the composition of the boron trichloride on distillation. By a fortunate accident, the quantity of boron trichloride in the final main fraction of the vacuum distillations of Series B and C had been much more than sufficient to fill eight bulbs, and the excess in each case had been collected as a *middle* fraction (M.F.B. and M.F.C.) in a large bulb provided with a special joint. Therefore it was determined to transfer these fractions to weighed bulbs by pouring in the manner described on p. 708, whereby, evidently, the fraction as a whole was subjected to an efficient separation from any less volatile impurity and yet any effect of distillation in causing a variation in the composition of the contents of individual bulbs was minimised. The effect of this is apparent in the average deviation from the mean in Final Series B and C, as contrasted with the corresponding figures for the Main Series A, B, and especially C. Evidently the nature and extent of the variations in the Final Series indicate that none of the analyses is likely to give an atomic weight in error by more than 0·005 and that most of the results are probably within 0·002 or 0·003 of the truth.

This being so, it follows that certain systematic variations apparent in the figures are *real* and require explanation. Three types of systematic variation may be distinguished in discussion:

(1) The last results in each series are high and in one case show a progressive increase.

(2) The first few values in each series diminish progressively to a minimum.

(3) The results in both the Main and the Final Series C are consistently higher than those in Series A and B.

Attention may first be directed to the possible impurities and their effect as illustrated by the data in Table I. The table is not exhaustive, as the possible impurities less volatile than boron trichloride clearly include higher chlorides of silicon, arsenic, phosphorus, etc., and also such compounds as chloroform and carbon tetrachloride, which, being non-hydrolysable under the conditions of analysis, would probably act, like boric oxide, as inert diluents. It is immediately evident that all impurities *less volatile* than boron trichloride tend to *increase* the apparent atomic weight, whilst chlorine and hydrogen chloride, both *more volatile*

than boron trichloride, tend to *diminish* the apparent atomic weight.

The negative results of tests for silicon and phosphorus in the later tail fractions obtained in the course of purification would seem to ensure that the final main fractions could not have contained any less volatile chloride in an amount sufficient to have any perceptible effect on the atomic weight. There is not the same conclusive evidence that boric oxide was eliminated: visible traces of the gummy residue (although so small as to appear unweighable) were seen at late stages of the purification, and it seems reasonable to suppose that the increase at the ends of the series may be due to traces of boric oxide concentrated in the later fractions. This view accounts satisfactorily for the abnormally high values at the end of Main Series C, as this was much the *longest* series (the middle fraction M.F.C. being large) and the final bulbs in this case contained a considerably smaller fraction of the whole than did the corresponding bulbs in the other series.

The progressive decrease in the earlier values in the series cannot, apparently, be attributed to the presence of impurities. The concentration of volatile impurities would be greatest in the head fractions and would progressively diminish: their presence tends to lower the atomic weight, and therefore would cause a progressive *rise* in the value obtained with successive fractions. This consideration and the apparent efficacy of the chemical means used to eliminate chlorine and hydrogen chloride indicate that another explanation of this drift must be sought.

It is, we believe, to be found in the hypothesis that an isotopic separation has occurred. During the distillation into bulbs, in order to keep the pressure in the apparatus well below atmospheric pressure, the main bulk of boron trichloride was kept at or near the freezing point and the bulbs were cooled in liquid air. Under these conditions, the distillation must have been largely irreversible and, therefore, likely to effect such a separation.

Neglecting the doubtful isotope of chlorine, Cl^{39}, the elements concerned have each two isotopes and may conceivably form the eight compounds formulated below with their molecular weights and the percentage of chlorine they contain.

Compound.	Mol. wt.	% Cl.
$B^{10}Cl_3^{35}$	115	91·4
$B^{11}Cl_3^{35}$	116	90·6
$B^{10}Cl_2^{35}Cl^{37}$	117	91·5
$B^{11}Cl_2^{35}Cl^{37}$	118	90·7
$B^{10}Cl^{35}Cl_2^{37}$	119	91·6
$B^{11}Cl^{35}Cl_2^{37}$	120	90·8
$B^{10}Cl_3^{37}$	121	91·7
$B^{11}Cl_3^{37}$	122	91·0

The lighter members of this group of compounds contain, for a given isotope of boron, a smaller percentage of chlorine than the corresponding heavier members : an increased weight percentage of chlorine causes an apparent diminution of the atomic weight : therefore a preponderance of the lighter compounds in the earlier fractions would account for the observed effect.

It should be remarked that separation in this order is determined by the difference in weight between the isotopes of chlorine. If the phenomenon under discussion is real and is due to a separation of compounds of isotopes, this order of separation affords definite evidence that in the great majority of molecules of these compounds the chlorine atoms are uniquely and permanently attached to their respective boron atoms. For if this were not so and, as is conceivable, chlorine atoms could migrate freely from one molecule of boron trichloride to another, then it is clear that for any group of B^{10} and B^{11} atoms, the chlorine in combination with either the lighter or the heavier boron atoms would, at any instant, have the same statistical average atomic weight, so that any separation by irreversible distillation would be determined solely by the relative weight of the boron atoms and would yield a series of fractions in which the atomic weight of boron would progressively increase.

This conclusion is in agreement with the work of von Hevesy and Zechmeister (*Ber.*, 1920, **53**, [*B*], 410), who have found that certain organic lead compounds in non-ionising solvents are not rendered radioactive by admixture with active lead chloride and hence conclude that no interchange of lead atoms can occur in the molecules of these compounds.

The difference in the final mean results for the three series merits more detailed consideration. The Preliminary Series and Main Series A exhibit a comparatively large variation : if the foregoing hypothesis be true, this may have been caused by a specially slow and cautious distillation of the boron trichloride in these cases, and it would follow that the values about the middle of the series should be nearest the truth. Because M 2 yielded a high value and M 6 was lost, some uncertainty attaches to any deduction from Main Series A : having regard to the effect of the middle fraction M.F.A., we are of opinion that it indicates an atomic weight about 10·825 for the Tuscany boron. Excluding the value for M 2, the mean is 10·834 with a probable error $\pm$ 0·005.

Much more definite conclusions may be drawn with regard to Series B and C. Main Series B is very consistent, the result, 10·819, probable error $\pm$ 0·0014, is scarcely changed (to 10·818, p. e. $\pm$ 0·0013) if the result M 10 is rejected.

After another distillation, the middle fraction yielded the three results of Final Series B, giving the mean value 10·818, p. e. ± 0·0008. Combining these results, we obtain the value B = 10·8183.

Main Series C is less concordant, but the explanation above suggested for the high values of M 25 and M 26 seems to justify their exclusion: the mean for the remaining four determinations is 10·841, p. e. ± 0·003: the mean including M 25 and M 26 is 10·855, p. e. ± 0·003. In this case the middle fraction, M.F.C., was much larger and gave the six concordant values of Final Series C, giving in mean 10·840, p. e. ± 0·002. Combining these results, we obtain substantially the same result, 10·8403 or 10·8407 respectively, whether the results of M 25 and M 26 are rejected or retained.

While this investigation was in progress, two other determinations of the atomic weight of boron have been published. Baxter and Scott (*Science*, 1921, **54**, 524) have stated that preliminary results obtained by the measurement of the ratios $BCl_3 : 3Ag$ and $BBr_3 : 3Ag$ indicated an atomic weight 10·83 ± 0·01. Their results have not been published in detail and cannot, therefore, be discussed in relation to our own: it is possibly significant that their result, probably obtained with boron of American origin, is comparatively high.

Hönigschmid and Birckenbach (*Ber.*, 1923, **56**, [*B*], 1467) determined the ratios $BCl_3 : 3Ag$ and $BCl_3 : 3AgCl$, using three samples of boron trichloride purified by fractional distillation in a vacuum by Stock and Kuss (*ibid.*, p. 1463). Unfortunately, the origin of their samples was, apparently, unknown. Sample I was derived from 40 c.c. of boron trichloride prepared (from boron and chlorine) and used by Stock, sometime prior to 1914, for the determination of certain physical constants (Stock and Priess, *Ber.*, 1914, **47**, 3109). Sample II was redistilled from 30 c.c. of crude material, newly made by the same method. Sample III was obtained from 50 c.c. of commercial boron trichloride. With these materials Hönigschmid and Birckenbach found the values (I) B = 10·840, (II) B = 10·818, (III) B = 10·825, which compare in striking fashion with the three results now recorded.

In calculating their final mean result, B = 10·820, they reject entirely the result B = 10·840, alleging that sample I had stood 4 months in the bulbs previous to analysis, and might have acted on the glass. In the course of our work we have repeatedly had clear evidence that no such action occurs, and our analyses, being spread, in the case of any given series, over several months, afford many clear proofs that such standing in sealed bulbs has no appre-

ciable effect on the apparent atomic weight. Moreover, it is difficult to see how, even if some corrosion of the glass occurred, it should affect the results.

Sample I should have been the purest of the three, since it was prepared from refined material, while samples II and III were prepared from crude material by a precisely similar process. Moreover, the data obtained with Sample I are, as a series, as consistent and apparently trustworthy as those for the other samples. The rejection of the result 10·840 deduced from Series I cannot, therefore, be justified unless solely on the ground of its discordance with the other results.

Thus it appears that, though they were made with much smaller quantities of material and that, perhaps, less rigorously purified than our own, the analyses of Hönigschmid and Birckenbach confirm our finding that different samples of boron may give values for the atomic weight differing by an amount much greater than any conceivable error of the determinations. We are informed by Messrs. Borax Consolidated Ltd. that, " generally speaking, prior to 1914, boron crude materials used in Austria and Germany were boracite from Sultan Tchair (Asia Minor) or borate of lime from South America." Thus there is a certain probability that the sample (made prior to 1914) for which Hönigschmid and Birckenbach obtained the value 10·840 was derived from an American source.

The obvious conclusion from our results, thus supported, is that boron from California has an atomic weight, B = 10·840, higher by 0·02 than that of boron from Asia Minor, B = 10·820. If our interpretation of the results of Series A is correct, the boron from Tuscany (B = 10·825) is similar to that from Asia Minor.

These values indicate that the American boron contains 84% and the Eurasian boron 82% of the heavier isotope.

Comparatively few earlier investigations afford any evidence for or against the possibility of such a variation in isotope ratio as is here indicated. Substantially identical results have been found for terrestrial and meteoritic iron, nickel, and cobalt (Iron : Baxter and Thorvaldson, *J. Amer. Chem. Soc.*, 1911, **33**, 337; Baxter and Hoover, *ibid.*, 1912, **34**, 1657. Nickel : Baxter and Parsons, *ibid.*, 1921, **43**, 507; Baxter and Hilton, *ibid.*, 1923, **45**, 694. Cobalt : Baxter and Dorcas, *ibid.*, 1924, **46**, 357) and in comparing chlorine from sea water with that in several minerals (Mlle I. Curie, *Compt. rend.*, 1921, **172**, 1025) and especially with that in the ancient mineral apatite from Balme (Mlle E. Gleditsch and B. Samdahl, *ibid.*, 1922, **174**, 746).

Brönsted and Hevesy (*Nature*, 1922, **109**, 813) prepared and purified mercury from 9 minerals, from as many different sources

in Europe and America, and compared the densities of these samples: they found no variation greater than the possible experimental error, corresponding to a variation of about 0·0012 in the atomic weight. More recently, Jaeger and Dijkstra (*Proc. K. Akad. Wetensch. Amsterdam*, 1924, **27**, 393) have compared the densities of samples of tetraethylsilicane prepared from twelve different sources, six meteoritic and six terrestrial, and found no evidence thus of any variation exceeding about 0·001 unit in the atomic weight of silicon.

Munro (J., 1922, **121**, 986) attempted to compare the equivalent weight of borax from the Hanmer Hot Springs, South Island, New Zealand, with that of ordinary commercial borax and could detect no difference. Unfortunately, his work is open to very serious criticism: the weights of borax were very small; the method of ascertaining this weight, by dissolving a *part* of a weighed mass of fused borax and again fusing and weighing the remainder, is objectionable; and the measurement of the *volume* of acid required for neutralisation is insufficiently precise. Further, as we have shown that fused borax is variable in composition, Munro's work must be rejected entirely.

On the other hand, Mlle Curie (*loc. cit.*) has found a value slightly above the normal for chlorine obtained from a Central African desert region, and Muzaffar (*J. Amer. Chem. Soc.*, 1923, **45**, 2009) has reported widely different atomic weights, 121·720, 122·374, 121·563, and 121·144 respectively, for samples of antimony extracted from stibnites from Peru, Bolivia, Borneo, and Hungary. Unfortunately, the method used in the latter determinations seems unsuited to precise work and does not inspire confidence in these results; and the excellent determinations of the ratio $SbCl_3:3Ag$ recently published (Sb = 121·77, Willard and McAlpine, *J. Amer. Chem. Soc.*, 1921, **43**, 797; Sb = 121·76, Hönigschmid, Zintl, and Linhard, *Z. anorg. Chem.*, 1924, **136**, 257; Sb = 121·748, Weatherill, *J. Amer. Chem. Soc.*, 1924, **46**, 2437) were made with material of unknown origin and cannot be related to Muzaffar's results.

It would seem that this evidence as a whole may be held to show that there is no inherent improbability in the variation in atomic weight now observed. It remains to be ascertained whether that variation is due to changes in the isotope ratio occurring through processes of solution, fusion, crystallisation, and volatilization occurring in the earth's crust (it may be noted that in most cases boron has probably been concentrated in the existing deposits by volatilisation, as boric acid, in steam), or whether, as Aston has suggested (*Ann. Rep.*, 1922, **19**, 272), the isotope-ratio was fixed at an earlier stage in the history of the element, possibly at the

time of its formation. In the latter case, it is to be anticipated that differences in atomic weight would be most evident, as in the present case, between samples from sources so widely separated in distance that little, if any, admixture can have occurred between them.

Evidently, to answer the question here raised, more, and more precise, data are needed as to the atomic weights of elements from known sources. We therefore urge upon all who determine atomic weights that they should use only materials of definite and known origin and should seek results of the greatest possible precision, so that all such determinations may contribute in some measure to a solution of this fundamental problem of the origin of the elements.

The broad conclusions that may be drawn from this investigation may now be summarised. The present analyses agree with those of Baxter and Scott and of Hönigschmid and Birckenbach in showing that the atomic weight of boron is less than 10·85 and therefore in requiring the rejection, which we have elsewhere justified on other grounds (Briscoe, Robinson, and Stephenson, *loc. cit.*), of all the results based upon the analysis of fused borax. Two samples of boron, derived from Europe and Asia Minor, have atomic weights approximating closely to the rounded mean value *10·82*, in agreement with Hönigschmid and Birckenbach; while a sample of boron derived from North American deposits gives for the atomic weight the rounded mean value *10·84*.

The authors desire to acknowledge a grant from the Research Fund of the Chemical Society which has defrayed part of the cost of this investigation, and to express their thanks to Captain F. P. Mills, of the Northumberland and Durham Rescue Brigade, for kindly supplying the liquid air used in the distillation of boron trichloride.

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NEWCASTLE-UPON-TYNE. [*Received, January 13th*, 1925.]

C.—*The Alternation in Molecular Volume of the Normal Monobasic Fatty Acids.*

By WILLIAM EDWARD GARNER and ERIC ALLITT RYDER.

PREVIOUS to this work, no measurements had been made of molecular volumes of the higher aliphatic acids in the solid state, and the published data for these acids in the liquid state were so fragmentary that it was difficult to decide to what extent alternation occurs in this property. Pauly (*Z. anorg. Chem.*, 1921, **119**, 278)

has summarised the known values for the acids with 1 to 8 carbon atoms and claims that a slight, although definite, alteration is observable in the molecular volumes of the liquids at the melting points. This behaviour would, however, be expected, since the melting points are alternating temperatures.

Randall and one of us (J., 1923, **123**, 881) have shown that the heats of fusion of that form of the solid acids stable at the melting point show a marked alternation as the homologous series is ascended (see Fig. 1) and have concluded that this alternation is intimately related to the atomic arrangement of the odd and even acids in the unit crystal cell, the length of which alternates from member to member.

From the work of Müller and Shearer (J., 1923, **123**, 2043, 3152), the unit cell contains 2 mols. of acid arranged end on end with their carboxyl groups in juxtaposition. Of the dimensions of this cell, only a perpendicular length between the carboxyl planes has been definitely established, and this, for the even acids, increases in a regular manner as the length of chain increases by two CH_2 groups. The odd members gave irregular results, very possibly on account of the occurrence of two crystalline forms of these acids which undergo transition one into the other comparatively slowly.

Other spacings, *viz.*, 3·7 and 4·1 Å.U., were observed to be the same for both the odd and the even acids, but the significance of these is not clear, no clue being afforded from the *X*-ray measurements to the actual area of cross section of the unit cell. The volume of the cell cannot at present be calculated without a knowledge of the molecular volumes in the solid state. These molecular volumes together with those for the liquid state have now been determined for the five acids from octoic to lauric (Table I). They are given for 50° for the liquid state, and for 15° for the solid state. For the liquids, a constant increase of 16·8 c.c. per g.-mol. occurs for each CH_2 added to the chain. The temperature coefficient of the molecular volume (Table V) does not change materially from acid to acid; thus, when measured at constant temperature, the molecular volume of the liquids must be a non-alternating property.

For the even acids in the solid state an increment of 27·5 c.c. per $2CH_2$ is obtained; but it will be noted that the molecular volumes of the odd acids in the solid state are greater than the mean of those of the even acids immediately above and below them in the series. Alternation therefore occurs in the molecular volume in the solid state and also in the volume change on fusion. The latter are plotted in Fig. 1 against the number of carbon atoms, and compared with the heats of crystallisation for the same acids. The values of the volume change on fusion lie on two curves, one for the odd

and the other for the even acids. That for β-undecoic acid lies just above the curve joining the values for the α-even acids, an analogous behaviour to that observed previously for the heats of crystallisation (Garner and Randall, *loc. cit.*).

FIG. 1.

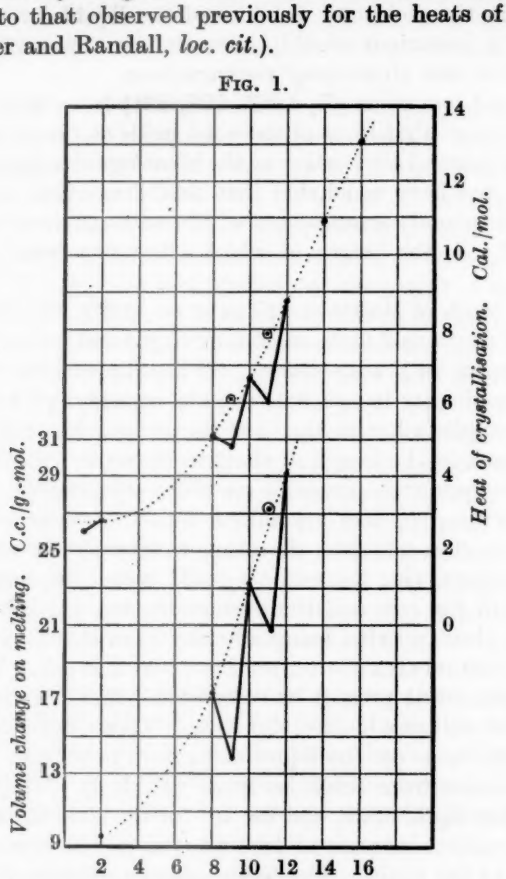


TABLE I.

Acid.	Mol. vol. of liquid in c.c./g.-mol. at 50°.	Δ c.c.	Mol. vol. of solid in c.c./g.-mol. at 15°.	Δ c.c.	*d* Å.U.	*S.* sq. Å.U.
Octoic	162·61		140·2		9·5	24·4
		16·82		19·9		
Nonoic (α)	179·43		160·1		11·45	23·1
		16·77		7·7		
Decoic	196·20		167·8		11·65	23·8
		16·75		18·7		
Undecoic (α)	212·95		186·5		12·9	23·9
		16·89		8·7		
Lauric	229·84		195·2		13·5	23·9
Undecoic (β)			180·0			
Acetic			47·4 *		3·33	23·5

* De Visser (*Rec. trav. chim.*, 1893, **12**, 139).

Area of Cross Section of the Unit Cell.—This may be calculated from the formulæ: (1) $S = MV/6{\cdot}06d \times 10^{-15}$ sq. Å.U., where d is the length of one molecule in the crystal cell, or from (2) $S = \Delta MV/6{\cdot}06 \times 2{\cdot}05 \times 10^{-15}$ sq. Å.U., ΔMV being the experimental increment in molecular volume for two CH_2 groups, and 2·05 Å.U. being the length of two CH_2 groups, when measured perpendicularly to the carboxyl planes. Those calculated by the former method (column 7, Table I), employing the experimental values for d of Müller and Shearer (*loc. cit.*) and of Gibbs (J., 1924, **125**, 2622), are identical for both the odd and the even acids within the experimental error of the two sets of figures. Even for acetic acid, of which de Visser (*loc. cit.*) gives values for the solid state, the same value of S is obtained. It thus follows that the area of cross section of the unit cell is a non-alternating property. Calculated by method (2), somewhat lower values are obtained, *viz.*, 22·4, 22·2, and 21·3 sq. Å.U. The cause of the discrepancy between the means of the two sets of figures (means 23·8 and 22·0 sq. Å.U., respectively) is not clear. The experimental errors in the quantities employed in the second calculation, *viz.*, in ΔMV and in the value 2·05 Å.U. for the length of two CH_2 groups, are probably greater than those in method 1. If the value for two CH_2 groups is reduced to 1·9 Å.U., the discrepancy disappears.

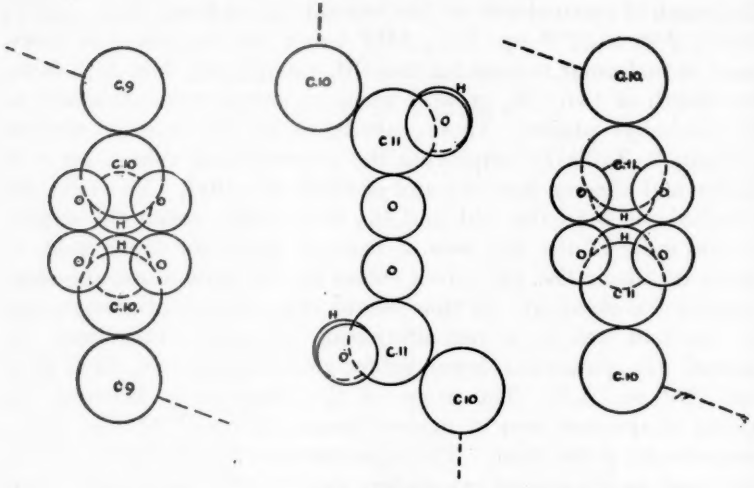
The area 23·8 sq. Å.U. is surprisingly large, being greater than the area deduced by Adam (*Proc. Roy. Soc.*, 1922, [*A*], **101**, 463) for the cross section of the molecules of these acids as packed in films on water, *viz.*, 21 sq. Å.U.

The structure of the crystal must be extremely open, if this be the correct cross section for the unit cell.

Calculated Length of the Crystal Cell.—The length of crystal cell containing two molecules, $2d$, may be obtained (1) from the formula $d = MV \times 2{\cdot}05/\Delta MV$, or (2) from the atomic diameters, C = 1·54, H = 1·15, and O = 1·15 Å.U., respectively (Yardley, *Proc. Roy. Soc.*, 1924, [*A*], **105**, 466), assuming the structures put forward by Müller and Shearer (*loc. cit.*) and later applied by Garner and Randall to the even and α- and β-odd acids. In the calculations made under (2), it has been assumed that the tetrahedral angle for the valencies of the carbon atoms is maintained in all cases. In the detailed analysis which has been made of the possible positions of the atoms in the carboxyl and methyl planes, only one of the possible arrangements for each acid gave a length of chain in agreement with the experimental results of Müller and Shearer. These configurations are given in Fig. 2. It will be seen that the hydrogen atom of the carboxyl group is assumed not to add to the length of chain. The arrangement of the carbon atoms in the chain (not

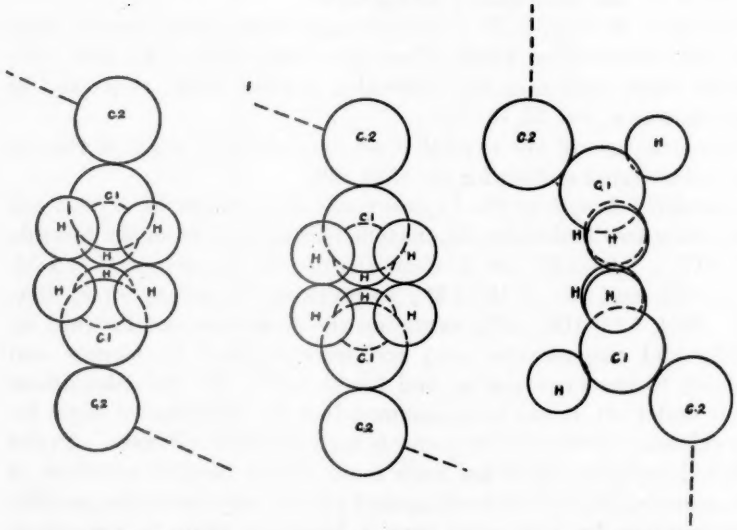
FIG. 2.

Carboxyl group.



Even acid. *α-Odd acid.* *β-Odd acid.*

Methyl group.



Even acid. *α-Odd acid.* *β-Odd acid.*

shown) is such that each $2CH_2$ adds 2·05 Å.U. to the length of the cell. The results obtained by methods (1), (2), and the experimental results of Müller and Shearer, and of Gibbs are given in Tables II

and III. In the first place, it will be noted that there is a constant difference between the values obtained by method (1) and the experimental results,* but that the latter agree with those obtained by method (2). If $\Delta 2CH_2 = 2{\cdot}0$ Å.U., the results by the three methods agree better; but those by the formula $d = MV \times 2{\cdot}0/\Delta MV$ are still about 0·7 Å.U. too high. This is practically the half diameter of a hydrogen or oxygen atom, and it is not improbable that a hydrogen atom should be interposed between the two carboxyl groups—Fig. 2, and that the lengths of unit cell, $2d$, given by Müller and Shearer should be increased by the diameter of a hydrogen atom.

Alternation in Length of Chain.—The differences between successive members in the series given in Table II are free from the above objections, as they are the same for both methods of calculation. Thus it will be noted that columns 3 and 5 show good agreement. For the members with 8 to 12 carbon atoms the increase in chain length on passing from an even acid to an α-odd is 1·4 Å.U. and to a β-odd acid 0·8—0·9 Å.U. Since the differences in column 3 are based on the experimental molecular volumes and those in column 5 on the structures postulated previously (J., 1924, 125, 885) for the α- and β-odd acids in the solid state, the above agreement is an indication that these structures are at least approximately correct. The experimental values of Müller and Shearer and of Gibbs (column 7) are in approximate agreement with these values, but, as it is uncertain which form of the odd acid they employed in their work, a general comparison for the whole series is not possible.

TABLE II.

Length of Chain of Monobasic Fatty Acids.

Acids. No. of carbon atoms.	Method 1.		Method 2.		Experimental.	
	d.	Δ.	*d*.	Δ.	*d*.	Δ.
8	10·45		9·75		9·5	
		1·48		1·40		1·95
9 (α)	11·93		11·15		11·45	
		0·58		0·65		0·20
10	12·51		11·80		11·65	
		1·39		1·40		1·25
11 (α)	13·90		13·20		12·9	
		0·65		0·65		0·60
12	14·55		13·85		13·5	
10	12·51		11·80			
		0·91		0·81		
11 (β)	13·42		12·61			

TABLE III.

Length of Chain of Even Acids.

No. of carbon atoms.	2	4	6	8	10	12	14	16	18	20
Experimental (M, S, and G)	3·33	4·83	7·3	9·5	11·65	13·5	16·1	17·35	19·35	23·9
Calculated (Method 2)	3·58	5·63	7·68	9·73	11·78	13·83	15·88	17·93	19·98	24·08

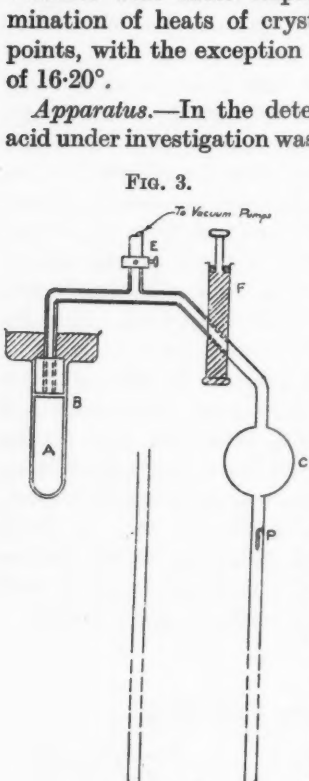
* Nonoic acid is somewhat abnormal.

EXPERIMENTAL.

Materials.—The acids used for the determination of molecular volumes were those employed previously (*loc. cit.*) for the determination of heats of crystallisation. They had the same setting points, with the exception of octoic acid, which had a setting point of 16·20°.

Apparatus.—In the determination of the specific volumes, the acid under investigation was placed in the bulb of an air thermometer.

FIG. 3.



The total volume of the bulb empty and the volume of the space not occupied by acid were determined by introducing known volumes of dry air from a gas burette to the evacuated bulb and measuring the resulting pressures. The gas burette, C, and the bulb, B, are shown in Fig. 3. For convenience in handling, the acids were weighed in a glass vessel, A, which made a sliding fit in the bulb, B. The latter was fitted with a carefully ground stopper with a mercury seal and connected with the gas burette and a mercury pump giving a vacuum of 10^{-5} mm. The bulb and burette were rigidly fixed in position in a copper thermostat, and connexion with a mercury manometer, D, was made through one of the sides of the copper tank. The pressures were read by means of a cathetometer supplied by the Cambridge Instrument Company and capable of reading to 1/100 mm.

Calibration of Gas Burette and Bulb.—The volume of the burette down to the pointer, P, was calibrated by means of mercury, and that of the bulb and its exit tubes by partly filling with a known weight of mercury and determining the remaining free space with air introduced from the burette. The volume of the gas burette was 8·1383 c.c. and that of the bulb 12·9185 c.c. at 19°. The accuracy of these measurements was about 1 part in 4000 and 1 part in 10,000 parts, respectively. Corrections were made for the temperature of different parts of the apparatus, coefficient of expansion of the glass scale and mercury columns, and the usual barometer corrections were made. Since the errors in the specific

volumes were ultimately found to be at least as high as 1 in 500, it is unnecessary to specify the nature of these in detail.

Details of Procedure.—After placing the acid in the bulb of the air thermometer, it was subjected to a preliminary treatment under a vacuum, to remove dissolved air, at a temperature higher than any of the temperatures at which measurements were made. It was then crystallised in a vacuum and cooled to 0°, or below, with the object of producing fine cracks throughout the solid and breaking down any vacuoles that might have been formed. If these precautions were not adopted, erratic results were obtained. Traces of moisture were removed by subjecting the solid to a high vacuum for 2 hours. Since the vapour pressures of the acids under the conditions of the experiments were low, there was no appreciable loss by evaporation; 7·75 g. of octoic acid decreased in weight only 0·0004 g. after a long series of investigations. Before carrying out a measurement, the acid was brought to the required temperature within 0·1°, and a known volume of dry air introduced into the gas burette at about atmospheric pressure, and after it had attained the temperature of the bath, the mercury level was adjusted to the pointer, P, by moving the mercury upwards. Providing no leak developed, the manometer readings, barometric pressure, etc., were then taken. This air was then admitted into the thermometer bulb, the mercury brought up to the pointer, and a reading of the pressure made as soon as possible. Since the equilibrium pressure was not attained until after about 20 minutes, these readings were repeated every few minutes, until no further movement of the mercury was observed. The slow disappearance of air was not due to the same causes in the cases of the liquid and the solid acids. Since the fall in pressure did not occur when the acid was replaced by mercury, it seems clear that the slow change in the case of the liquids was due to solution of air in the surface layers. The value for the volume of the free space, used for the calculation of the specific volume of the liquids, was therefore obtained by extrapolation back to the time of admission of air. The difference in the pressure between the maximum and the initial readings was never more than 2 in 1000, so that the error in the initial reading is unlikely to be large. For the solids, the change in pressure with time was less the more thoroughly the acid was broken up by cooling, thus it cannot be ascribed to absorption on the solid surface. Further evidence in support of this contention was found in the case of undecoic acid, where a complete series of determinations was made during which the equilibrium pressure was attained immediately after admitting the gas. In a number of others, however, the change in pressure was several mm. on a pressure

of about 500 mm. The α-nonoic acid gave the most trouble, and on this account the values for this acid are thought to be less accurate than the others. The change in pressure is most probably caused by the presence of vacuoles which are connected with the surface by a series of fine cracks. Hence the equilibrium pressure was taken for the calculations of the specific volumes in the solid state. The values obtained after melting and resolidifying were identical with those obtained for the first series at the same temperature to within 2 in 1,000.

TABLE IV.

Densities and Specific Volumes (Air Thermometer Method).

Acid.	Wt. (g.).	Temp.	Density.	Specific volume.	Temp. coeff. per 1°.
Octoic	7·7564	10·0°	1·0326	0·9685	0·00098
		15	1·0274	0·9733	
		20	0·9109	1·0979	0·00046
		25	0·9090	1·1002	
Nonoic	7·1509	5·0	0·9952	1·0048	0·00074
		10	0·9916	1·0085	
	7·6853	15	0·9097	1·0993	0·00104
		25	0·9011	1·1097	
Decoic	7·7308	15·0	1·0266	0·9741	0·00085
		25	1·0176	0·9827	
		35	0·8927	1·1202	0·00128
		40	0·8876	1·1266	
Undecoic	7·7713	0·12	1·0431	0·9587	0·00054
		10·0	1·0373	0·9640	
		20	0·9948	1·0052	0·00079
		25	0·9905	1·0096	
		30	0·8907	1·1227	0·00093
		35	0·8871	1·1273	
Lauric	8·3722	35·0	1·0099	0·9902	0·00087
		40	1·0055	0·9945	
		45	0·8767	1·1406	0·00142
		50	0·8713	1·1477	

Results.—The specific volumes were measured at two temperatures for each phase, and from three to five determinations were made at each temperature. At the end of a series over a range in temperatures, the experiments at the first temperature were repeated, and it was found that no drift in the values occurred due to changes in the experimental conditions. To test the method, several series of determinations were made with α-undecoic acid. The means are given in Table IV.

The densities of the acids in the liquid state have also been determined in a pyknometer of volume 5·0470 c.c. at 30°. The experimental results for two temperatures, one as near the melting point as possible, are given in Table V.

Table VI embodies the results obtained by both air thermometer and pyknometer methods for the specific volumes of the solid and

TABLE V.

Acid.	Temp.	Wt. of acid in air (g.).	Density.	Temp. coeff.
Octoic	50·27°	4·4738	0·8862	0·00099
	20·02	4·5923	0·9101	
Nonoic	50·17	4·4491	0·8813	0·00097
	15·00	4·5842	0·9087	
Decoic	50·17	4·4290	0·8773	0·00095
	35·05	4·4834	0·8884	
Undecoic	50·15	4·4129	0·8741	0·00095
	30·00	4·4856	0·8889	
Lauric	50·25	4·3957	0·8707	0·00095
	45·10	4·4140	0·8744	

liquid acids at the melting point and, for the liquid acids, at 50°. In addition, the change in molecular volume on melting is included. Those by the air thermometer method have been obtained for each phase from the results in Table IV, by taking the means for the two temperatures given, and applying to these values the mean temperature coefficients given below.

TABLE VI.

		Octoic.	Nonoic.	Decoic.	Undecoic.	Lauric.
Specific volumes.	*Solid, M. Pt.* (air thermometer).	0·9737	1·0104	0·9870	1·0121	0·9971
	Liquid, M. Pt. (air thermometer).	1·0925	1·0966	1·1169	1·1206	1·1403
	Liquid 50° (pyknometer).	1·0951	1·0979	1·1220	1·1232	1·1423
	Liquid 50° (pyknometer).	1·1283	1·1347	1·1398	1·1440	1·1483
Molecular volumes.	ΔMV at M. Pt.	17·51	13·95	23·24	20·68	29·07

Mean temp. coeff. spec. vol. Solids : 0·00077 per 1°.
Liquids : 0·00103 per 1°.

In calculating the molecular volume change on melting, the pyknometer values of the liquid acids were used. Those by the air thermometer method appear to be in error by 2 parts in 1000. The molecular volume change on melting for β-undecoic acid, assuming that this acid melts at 28·5°, is 27·26 c.c./g. mol.

Summary.

The molecular volumes of octoic, α-nonoic, decoic, α- and β-undecoic, and lauric acids have been determined. Those for the liquid state at 50° increase by 16·8 c.c./g. mol. for each CH_2 group added to the chain, whereas those for the solid state alternate in a marked manner as the series is ascended. The area of cross section of one molecule in the crystal, 23·8 Å.U., is non-alternating, hence the alternation in molecular volume is due entirely to changes in the chain-length from member to member. The magnitude of the alternation is in agreement with the views expressed in a

previous paper (*loc. cit.*) with regard to the constitution of these acids in the solid state.

The authors wish to express their indebtedness to the Chemical Society for a grant towards the cost of the acids employed in this investigation.

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CI.—*The Interaction of Nitrogen Sulphide and Sulphur: Nitrogen Persulphide.*

By FRANCIS LAWRY USHER.

IN order to eliminate the last traces of free sulphur from nitrogen sulphide the crystals which separate from benzene * are usually sublimed in a vacuum over a roll of heated silver gauze at steam temperature (Burt and Usher, *Proc. Roy. Soc.*, 1911, [*A*], **85**, 82) On attempting to expedite this process by jacketing the sublimation tube with the vapour of a liquid of higher boiling point than water, namely, *iso*amyl alcohol, b. p. 124—125°/about 695 mm., a ruby-coloured film appeared almost immediately over about 2 feet of the glass tubing connecting the sublimation tube with the mercury pump. At the same time, nitrogen was evolved much more freely than usual, and the silver was rather thickly coated with silver sulphide. The sulphide at the bottom of the sublimation tube, which was subsequently found to be largely contaminated with sulphur, underwent partial fusion, and bubbles of gas or vapour escaped from it. As the sublimation proceeded, the ruby deposit increased in depth of colour, although always retaining its transparency except in the wider tubing just above the cork which fitted into the vapour jacket; on warming, it disappeared, and was condensed on adjacent parts of the tubing as a blue film. After about 2½ hours, the whole of the deposit became deep blue. During the experiment the phosphoric oxide above the pump was coloured a deep pink, whilst the metaphosphoric acid which accompanied it became bluish-green. On the next day, air was admitted to the apparatus, when the colour of the phosphoric oxide turned to a yellowish-red. On treating a portion of the oxide with water, the

* Crystallisation from carbon disulphide is more effective than crystallisation from benzene in removing sulphur. The best method (apart from sublimation in a vacuum over heated silver gauze) is, however, to shake a solution of the substance in either solvent with mercury for some time.

colour was slowly discharged, and a smell of sulphur dioxide was noticed; whilst from the remainder benzene extracted a small quantity of yellow, crystalline nitrogen sulphide.

This ruby-coloured substance, which was never obtained in quantity sufficient for analysis, was insoluble in all solvents tried, excepting those which altered it chemically, and in fact behaved precisely like the blue nitrogen sulphide described by Burt (J., 1910, **97**, 1171). On warming, it turned blue, slowly at 50°, rapidly at 60°; the product, judged by its appearance and behaviour, being almost certainly chemically identical with Burt's sulphide. No gas was evolved during the conversion of the ruby into the blue substance, and a careful microscopic examination of the tube after the conversion failed to reveal the presence of any other substance beside the blue sulphide: it is therefore concluded that the ruby substance has the same empirical composition as ordinary yellow nitrogen sulphide. The conversion of the ruby to the blue substance at the room temperature (23—30°) sometimes occurred within ½ hour and has never been observed to take more than 2 days.

None of the ruby compound was formed from the same raw material at steam temperature, although on substituting *iso*amyl alcohol for the water the deposit was formed as before, and nitrogen was freely evolved. In the course of a number of similar experiments, the phosphoric oxide was always coloured, but the colour varied: most frequently the oxide nearest to the sublimation tube was red, that next to it blue, the middle portion a pale greyish-blue, whilst the end nearest to the pump was pink.

A sample of nitrogen sulphide re-crystallised from carbon disulphide did not yield any of the ruby compound when sublimed over silver either at steam temperature or at 125°. At 128°, there was a larger yield than usual of the blue sulphide, and a considerable quantity of nitrogen was given off, but no ruby deposit. Finally, a specimen of nitrogen sulphide (0·2 g.) which had been purified by sublimation over silver gauze at steam temperature was re-sublimed at 139°, when only 1 c.c. of nitrogen was evolved, although there was the usual production of blue sulphide without any visible trace of the ruby variety. Two tubes of phosphoric oxide attached to the pump were coloured a deep greenish-blue, which by the next day had changed—without the admission of air—to deep yellow. At 124° only 0·077 c.c. of nitrogen was evolved during the sublimation of 0·25 g., although there was a marked production of the blue sulphide. Attempts to obtain the ruby sulphide from the blue variety were never successful. When an exhausted tube containing the blue sulphide was gradually heated, the substance sublimed unchanged, slowly at 140°, rapidly at 150—160°. At 165°, it was

partly decomposed, yielding a mixture of products among which could be detected two kinds of crystal, probably sulphur and ordinary nitrogen sulphide, together with a smaller amount of a reddish-brown liquid. When the whole tube was heated at 145°, the blue sulphide was all decomposed, yielding the same products as before. On treatment with various indifferent solvents, it either remained unchanged or dissolved in another form: thus in boiling mesitylene it dissolved, forming a yellow solution.

In order to ascertain definitely whether the presence of free sulphur in yellow nitrogen sulphide is necessary for the formation of the ruby product, a mixture of very pure (re-sublimed over silver) nitrogen sulphide with sulphur in the proportion NS : S was sublimed in a vacuum over silver gauze heated at 124—125°; the ruby film was produced just as in the previous experiments.

Nitrogen Persulphide.—The experiment last mentioned was repeated, with the omission of the silver gauze. The mixture of nitrogen sulphide and sulphur fused and emitted bubbles, while a red substance appeared over the tubing leading to the pump, excepting about 6 inches next to the sublimation tube, and condensed especially on portions which were cooled by a pad of wet cotton wool. By local cooling, the red substance, which was liquid, could be distilled from one part of the tubing to another. Nitrogen was freely evolved, although no silver was present. In a subsequent experiment, some of the substance was condensed by means of solid carbon dioxide and alcohol in a small glass bulb carrying two tubes, each of which was drawn down at one place to a capillary. After allowing the sublimation tube to cool so that no more nitrogen was evolved, the apparatus was thoroughly exhausted and the bulb sealed off. Preliminary trials had shown that the red substance could be completely decomposed into nitrogen and sulphur by heating for an hour in the vapour of boiling sulphur, and this method was selected for its analysis. Since only about 0·01 g. could be collected at a time, it was not possible to weigh the compound itself; the glass having to be scratched in order to open the bulb, the small amount of glass powder lost in this way or on breaking the tube would have introduced a relatively large error. To determine the weights of nitrogen and sulphur in an unknown weight of the compound, the sealed bulb was suspended in the vapour of boiling sulphur for 1 hour, after which one of the tubes, the capillary tip of which had been scratched with a glass knife, was attached to a mercury pump by means of a piece of thick-walled rubber tubing, and the system on the pump side of the bulb thoroughly evacuated. The scratched tip was then broken off inside the rubber tubing, and the gaseous contents of the bulb pumped off into a small tube filled

with mercury and inverted over the end of the discharge tube of the pump. This nitrogen was then transferred to a small, constant-volume gas burette and measured. The bulb containing the sulphur was next removed from the pump and both of its tubes were cut off below the capillary tips. It was then weighed on an Oertling assay balance, the sulphur being afterwards burnt out and the bulb weighed empty. The rider used on the assay balance belonged to the set of weight previously used in calibrating the constant-volume burette, and had been calibrated in terms of one of the weights. The following are the results of two analyses made in this way:

Vol. of nitrogen at N.T.P.	1·366 c.c.	1·378 c.c.
Weight of nitrogen	0·001709 g.	0·001724 g.
,, sulphur	0·00786 g.	0·00783 g.
Ratio S : N	2·05	1·98

The empirical formula of the compound is therefore NS_2, and it may conveniently be called *nitrogen persulphide*. The difficulty of collecting it in sufficient quantity precluded the determination of its molecular weight in solution, but some light was thrown on this matter during one of the earlier analyses, when the compound had been heated insufficiently. The nitrogen was collected and measured as already described, but on the next day the surface of the mercury in the constant-volume burette was observed to be slightly soiled, and on re-measuring the nitrogen the volume was found to have diminished by 0·016 c.c. The simplest explanation is that a small proportion of the sulphide had escaped decomposition and had been carried over as vapour with the nitrogen, being subsequently decomposed by prolonged contact with the mercury. In these circumstances, a diminution of volume could occur only if the compound contained one atom of nitrogen in its molecule, and it may therefore reasonably be surmised that the highly diluted vapour at the ordinary temperature has the formula NS_2.

The persulphide is liquid at the ordinary temperature, and has the appearance of bromine, being red in thin films and almost black in layers more than a millimetre thick. At the temperature of solid carbon dioxide it is a pale yellow solid. It can only be distilled without decomposition in a vacuum, and is much more volatile than N_4S_4. It has a penetrating smell, somewhat resembling that of iodine, and is readily soluble in benzene, chloroform, carbon disulphide, and ether. An ether solution when mixed with alcoholic potash gives an intense violet colour. It cannot be preserved at the ordinary temperature for more than a day, even in a vacuum, but decomposes slowly into solid products which on examination with a lens appear to be yellow nitrogen sulphide and sulphur. Water decomposes it, giving a mixture of products among which are

ammonium salts and free sulphur. Dry hydrogen sulphide passed into an ether solution produces some separation of sulphur, whilst the originally red liquid becomes almost colourless, and gives with ammonia a yellow precipitate which is soluble in absolute alcohol, but is immediately decomposed by water with separation of sulphur. These reactions could only be observed qualitatively on account of the paucity of material, but they perhaps suggest the formation of an unstable thio-acid of nitrogen.

Mode of Formation of the Volatile Sulphides.—The experiments described in this paper shed no very definite light on the chemistry of the formation of the modifications of ordinary nitrogen sulphide or of the persulphide, although they indicate clearly enough that the former certainly, and the latter possibly, are produced by decomposition of an intermediate compound not yet identified. It has been shown that the ruby sulphide is formed only when free sulphur is present in the yellow nitrogen sulphide, and when this material is sublimed over silver maintained at about 125°; whereas the blue modification is produced over a rather wider range of temperature, and does not require the presence of free sulphur. The view that the persulphide is formed by simple combination is negatived by the observation that nitrogen is freely evolved by the mixture at a temperature at which pure nitrogen sulphide remains quite undecomposed. Either nitrogen sulphide and sulphur interact with the production of the persulphide and nitrogen, or they combine to form a compound which subsequently decomposes into the persulphide and nitrogen. With regard to the blue sulphide, Burt (*loc. cit.*) has pointed out that it arises by the decomposition of a gaseous or at least a very volatile sulphide of unknown composition containing a larger proportion of nitrogen, and this is clearly also the case with the ruby sulphide, which is only formed in the presence of silver, and is always accompanied by a gaseous or very volatile product which reaches and colours phosphoric oxide connected with the sublimation tube by a considerable length of cold tubing. That this volatile substance is formed in appreciable quantity is proved by the possibility of extracting a visible amount of nitrogen sulphide from the phosphoric oxide; and it appears extremely probable that it is not chemically identical with the substance which gives rise to the blue sulphide, for if it were, the production of this or the ruby variety would be determined by conditions at the place where they were deposited rather than by the chemical composition of the parent material. All that can be stated with any confidence is that silver at temperatures from 100° to 140° decomposes ordinary nitrogen sulphide to a very slight extent, forming an unknown volatile product which gives rise to a blue modification; and that a

ruby modification is similarly produced from a different volatile compound which in turn arises by the decomposition by silver, within narrower temperature limits, of another sulphide, which is possibly nitrogen persulphide. There is thus evidence of the existence of at least two volatile sulphides of nitrogen of unknown composition.

Some reference must be made to the remarkable similarity of the properties of nitrogen persulphide to those of the substance prepared by Muthmann and Clever (*Z. anorg. Chem.*, 1897, **13**, 200) by heating a solution of ordinary nitrogen sulphide in carbon disulphide for some hours in a sealed tube, and stated by them to be nitrogen pentasulphide. Muthmann and Clever's substance has been prepared according to their directions, with the object of comparing its behaviour with that of the persulphide, and of attempting to purify it by distillation in a vacuum and analysing the distillate. A " clean " separation from the last traces of solvent by distillation was, however, impracticable with the small quantity of the substance available, and an analysis would therefore have been inconclusive: qualitatively, the resemblance between the two substances was complete. The author would tentatively suggest the possibility of Muthmann and Clever's " pentasulphide " having been a solution of sulphur in persulphide. Apart from the striking similarity in their properties, it may be pointed out that Muthmann and Clever inferred the purity of their material, which was obtained by evaporation of an ethereal solution, from their observation that free sulphur was almost insoluble in ether at the temperature employed by them. If, however, their product was really nitrogen persulphide, there is little doubt that an appreciable quantity of sulphur would have remained in the mixture of the persulphide with ether.

CENTRAL COLLEGE, BANGALORE. [*Received, January 13th*, 1925.]

CII.—*The Interaction of Sodium Chloride and Alumina.*

By FRANCIS HERBERT CLEWS.

SODIUM chloride is known to react with alumina and with silica in a similar manner. Tilghman (Brit. Pat. 11556, 1847), Gossage (*ibid.* 2050, 1862), Hargreaves (*ibid.* 2121, 1867), and Grüneberg and Vorster (*ibid.* 2639, 1874) were aware of the reaction in presence of moisture yielding sodium aluminate and hydrochloric acid, whilst De Lande and Prud'homme (*Bull. Soc. chim.*, 1872, [ii], **17**, 290) and Schultze (*J. pr. Chem.*, 1880, [ii], **21**, 407) observed

the reaction in presence of air or oxygen yielding sodium aluminate and chlorine. The subject was deemed worthy of a more quantitative investigation.

Experimental.

The heating element consisted of a nichrome-wound silica tube the temperature of which was controlled to $\pm$ 10° over long periods by means of an adjustable resistance in conjunction with an automatic regulator designed to overcome variations in temperature due to fluctuations in the voltage supplied. The furnace temperatures were measured by a standardised platinum–platinum rhodium thermocouple. The reactions were carried out in alundum* tubes which, being somewhat pervious to gases, were enclosed in a slightly larger silica tube.

Products and Course of the Reaction.—The following reactions have been observed :

(*a*) $4x\mathrm{NaCl} + y\mathrm{Al_2O_3} + x\mathrm{O_2} = 2x\mathrm{Na_2O},y\mathrm{Al_2O_3} + 2x\mathrm{Cl_2}$.
(*b*) $2x\mathrm{NaCl} + y\mathrm{Al_2O_3} + x\mathrm{H_2O} = x\mathrm{Na_2O},y\mathrm{Al_2O_3} + 2x\mathrm{HCl}$.
(*c*) $4\mathrm{HCl} + \mathrm{O_2} = 2\mathrm{H_2O} + 2\mathrm{Cl_2}$.

Reaction (*b*) is reversible at about 1000°. The formation of aluminium chloride has not been observed in these experiments, which have been restricted to reactions in the presence of water. This does not preclude its formation under anhydrous conditions.

Materials.—Pure, dry sodium chloride was used and the alumina was prepared by igniting recrystallised ammonium alum, free from iron, in a muffle, extracting for 2 days in a Soxhlet extractor with dilute hydrochloric acid, re-igniting in the muffle for 6 hours, followed by a fresh extraction for 2 days. The pulverulent product showed no traces of sulphate on testing after fusion with sodium carbonate.

Effect of Rate of Flow of Gas over the Reaction Mixture.—A purified stream of moist air was passed at a constant rate over 0·5 g. of a mixture of equal parts by weight of alumina and sodium chloride placed in a platinum boat and heated in the furnace in a silica-jacketed alundum tube. The gaseous products of the reaction were absorbed in a U tube filled with fragments of glass moistened with sodium bicarbonate and potassium iodide. The reaction tube was finally swept out with a current of dried air. The experiments were duplicated and the results are shown in Table I.

The results indicate that reaction (*b*) predominates, and that the chlorine produced is to be attributed more to reaction (*c*) than reaction (*a*), since it is dependent on the rate at which air and water

* 15·42% $\mathrm{SiO_2}$; 83·25% $\mathrm{Al_2O_3}$; 0·49% $\mathrm{Fe_2O_3}$; 0·52% $\mathrm{TiO_2}$; 0·76% CaO.

TABLE I.

Duration of experiment	5 hours.
Mean temperature of furnace	1009°.
Temperature of saturation of air with water vapour	50°.

C.c. of air passed.	Cl_2 (c.c. of $N/20$).	HCl (c.c. of $N/20$).	$\frac{Cl_2}{HCl}$	$\frac{Cl_2}{HCl + Cl_2}$
9400	10·8	74·6	0·145	0·126
8450	10·5	67·5	0·156	0·135
6500	18·5	63·9	0·290	0·225
3000	24·0	51·6	0·465	0·317
1600	26·2	49·9	0·525	0·344
1250	22·1	35·6	0·621	0·383
1050	17·9	37·4	0·479	0·324

are supplied. Examination of equation (*c*) shows that a proportionate increase in the concentration of water and oxygen would lead to a displacement of equilibrium to the left.

Effect of Proportion of Sodium Chloride and Alumina.—The results are shown in Table II.

TABLE II.

Duration of experiment	5 hours.
Volume of air passed	6500 c.c.
Temperature of saturation of air with water ...	50°.
Temperature of furnace	1009°.

0·5 G. of	HCl (c.c. of $N/20$).	Cl_2 (c.c. of $N/20$).	$\frac{Cl_2}{HCl + Cl_2}$
100% NaCl	64·6	16·4	0·202
75% NaCl	76·2	26·0	0·254
50% NaCl	63·9	18·5	0·225
25% NaCl	36·6	6·6	0·150

Effect of Temperature on Reaction (b).—0·5 Gram of an intimate mixture of equal weights of sodium chloride and alumina was heated as previously described in an atmosphere of water vapour produced by allowing water to drip at a very slow constant rate from a capillary tube into the silica tube. The hydrochloric acid produced was collected and titrated with $N/10$-alkali. Reactions (*a*) and (*c*) were excluded. The composition of the residue was determined by gravimetric analysis, the sodium oxide being determined by Smith's method (*Amer. J. Sci.*, 1871, [ii], **50**, 269).

At the higher temperature very little of the resulting sodium aluminate was soluble or hydrolysable. The results are summarised in Table III.

The results indicate that above 1000°, for a given quantity of sodium chloride, the reaction with alumina is virtually complete, as would be expected, since the method of supplying the water for the reaction precludes the reverse one.

In these experiments the amount of sodium oxide produced in the platinum boat was always less than that equivalent to the

TABLE III.

Duration of experiment ..... 5 hours.

Temp.	HCl (c.c. of $N/10$).	Composition of residue. % NaCl.	% Na_2O.	% Al_2O_3.	$\frac{Na_2O}{Al_2O_3}$
1075°	46·65	0·2	3·7	96·1	0·0385
1008	42·20	0·97	11·8	87·2	0·135
952	35·20	12·1	6·8	81·1	0·0838
897	29·55	—	—	—	—
838	20·30	32·3	5·5	62·2	0·0883
785	8·93	44·6	3·8	51·6	0·0737
707	3·35	—	—	—	—
605	0·50	—	—	—	—

hydrochloric acid absorbed, particularly at the higher temperatures. This is to be attributed to the reaction of sodium chloride vapour with the alundum tube in addition to the reaction of the unvolatilised reagents in the boat. Thus we find that the reaction at 1075°, although productive of the greatest yield of hydrochloric acid, does not give the greatest yield of sodium oxide in the residue.

Equilibrium Experiments.—(*A*). An attempt was now made to determine the effect of varying proportions of water and hydrogen chloride on the proportion of sodium chloride, sodium aluminate, and alumina in equilibrium with the vapours at a temperature (830°) where sodium chloride is not markedly volatile.

Equilibrium was approached from both sides. In one platinum boat was placed a mixture of equal weights of sodium chloride and alumina, and in another, a mixture of 40% sodium chloride, 40% alumina, and 20% sodium aluminate, made by previously calcining equal weights of alumina and sodium carbonate. The two boats were heated in a stream of water vapour and hydrogen chloride, obtained by allowing a solution of hydrochloric acid to drip slowly through a capillary tube into the silica reaction tube. A blank experiment with an empty tube showed that the acid condensing after passing through the furnace had the same composition as that entering it. The results showed that equilibrium was imperfectly attained in the solid mixtures, since differences of about 1% were obtained in the proportions of sodium oxide present. The results given in Table IV are mean values.

A noticeable feature is the almost constant proportion of sodium oxide in the solid mixture in equilibrium with the gaseous phase, irrespective of the composition of the latter.

(*B*). Similar experiments were made to ascertain the composition of the sodium aluminate in equilibrium with varying gaseous mixtures of hydrogen chloride and water vapour saturated with sodium chloride vapour at 1045°. The procedure was similar to that just described, but to render the alundum reaction tube inert

TABLE IV.

Mean temperature 829°.

Composition of gaseous phase.	Composition of solid phase.		
$\frac{[H_2O]}{[HCl]}$.	$\frac{[NaCl]}{[Al_2O_3]}$.	$\frac{[Na_2O]}{[Al_2O_3]}$.	$\frac{[NaCl]}{[Na_2O]}$.
57·4	1·65	0·067	24·6
505·0	1·64	0·080	20·5
2740·0	1·56	0·075	20·8
5480·0	1·53	0·074	20·7

to the gaseous reagents it was first treated with concentrated sodium hydroxide and dried. The boats were then introduced and heating was commenced in an atmosphere of the required composition. Thus the alundum tube as well as the contents of the two platinum boats was finally in equilibrium with the vapours. Equilibrium was assumed to be obtained when the composition of the condensed acid was the same as that of the original, which was usually after 20 to 24 hours' heating. Table V shows the results obtained.

TABLE V.

Mean temperature 1045°.

Composition of gaseous phase $[H_2O]/[HCl]$.					
13·7	27·6	66·9	105·0	529·0	1590·0
Composition of solid phase $[Na_2O]/[Al_2O_3]$.					
0·017	0·026	0·070	0·107	0·102	0·117

The stability of sodium aluminate with reference to hydrochloric acid decreases rapidly at 1045° when the molecular ratio Al_2O_3/Na_2O is less than 10 to 1 (see Table V), and at 830° when the ratio is less than 12 to 1 (see Table IV). In this reaction, no quantitative relationship between the composition of the gaseous phase and of the solid phase is apparent from these results. For the complete reaction of sodium chloride with alumina in the presence of water, an excess of alumina appears to be of greater moment than an excess of water.

I am indebted to Mr. H. V. Thompson, M.A., for suggestions and advice, and also to The Chemical Society for a grant which has partially defrayed the expenses incurred in the investigation

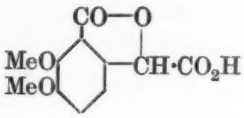
CENTRAL SCHOOL OF SCIENCE AND TECHNOLOGY,
STOKE-ON-TRENT. [*Received, February* 14*th*, 1925.]

CIII.—*A Synthesis of Oxyberberine.* Part I.*

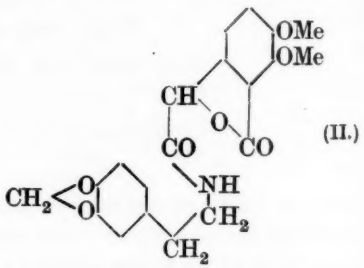
By WILLIAM HENRY PERKIN, jun., JANENDRA NATH RÂY, and ROBERT ROBINSON.

IN view of the recent work of Haworth, Perkin, and Rankin (J., 1924, **125**, 1686), it cannot be assumed that a synthetical proof of the constitution of berberine has yet been given and we have therefore decided to continue the investigation of this subject in several directions. A simple synthesis of oxyberberine has now been devised and in the present communication we place this on record, leaving the more complete description of an intermediate, at present employed in an unpurified condition, for a subsequent paper. Meconinecarboxylic acid (I) was synthesised by Fritsch (*Annalen*, 1898, **301**, 358) from *o*-veratric acid, and a simple method of preparation from opianic acid has been indicated by Robinson and Robinson (P., 1913, **29**, 267). The latter method was employed by Freundler (*Bull. Soc. chim.*, 1914, [iv], **15**, 465), who prepared numerous derivatives of the acid and among these the β-piperonylethylamide (II), m. p. 148°.

(I.)



(II.)



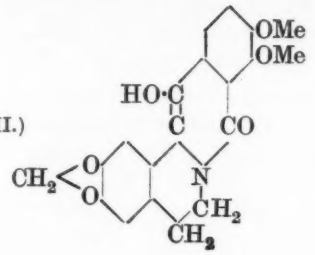
According to Freundler this substance is not converted into a dihydro*iso*quinoline derivative by the action of phosphoric anhydride or phosphoryl chloride, and we can confirm this statement if the treatment is of short duration. We found, however, that change did occur when the amide in phosphoryl chloride solution was heated during some hours on the steam-bath, and on adding the product to water an ochreous precipitate was obtained. This was to a large extent insoluble in boiling acetic acid, and the pale yellow residue, which could be crystallised from hot aniline, showed the highly characteristic reactions and properties of dioxyberberine (III) (Perkin, J., 1889, **55**, 1087).

This experiment was a preliminary trial and was made merely to determine whether reaction occurred at all. The conditions are not precisely known and on repetition, with larger amounts but in similar circumstances in other respects, different results were

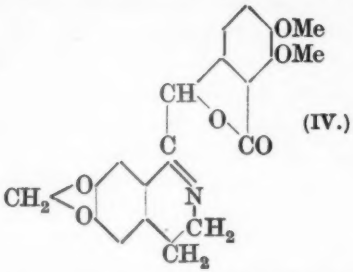
* Compare Pictet and Gams, *Ber.*, 1911, **44**, 2036.

obtained. The neutral product was produced in small relative amount and was not dioxyberberine, whilst the main product was a

(III.)

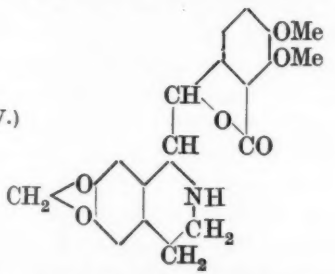


(IV.)

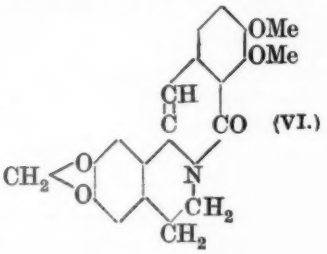


base which we regard as a dihydro*iso*quinoline (IV), although this is at present only a working hypothesis. When the entire basic product was treated with zinc dust in boiling acetic acid solution, oxyberberine (VI) was produced, possibly through the intermediate (V). Naturally the mechanism of the whole process will be further closely investigated, but whether the explanation which we now advance is subsequently justified or not, the synthesis establishes the correctness in important details of the constitution now generally assumed for oxyberberine and, in particular, a satisfactory proof of the position of the methoxyl groups is afforded.

(V.)



(VI.)



A synthesis of oxyberberine is also a synthesis of tetrahydroberberine and therefore of berberine, because oxyberberine has been shown to yield tetrahydroberberine when reduced electrolytically (Perkin, J., 1918, **118**, 764). Moreover, berberine is the starting point for the syntheses of other alkaloids, for example, canadine (Gadamer and Voss, *Arch. Pharm.*, 1910, **248**, 43) and palmatine (Späth and Lang, *Ber.*, 1921, **54**, [*B*], 3064).

Experimental.

Meconinecarboxylic Acid (I) *and its* β-*Piperonylethylamide* (II).—A mixture of opianic acid (20 g.), pure potassium cyanide (8 g.), and water (75 c.c.) was allowed to remain during 40 minutes and,

after the addition of 15% hydrochloric acid (60 c.c.), boiled during 12 minutes. α-Cyanomeconine (Robinson and Robinson, *loc. cit.*) separated from the hot solution as an oil, which readily crystallised on cooling the liquid. The substance was collected, washed with water, and hydrolysed by boiling with concentrated hydrochloric acid (60 c.c.) during 2 minutes. The liquid was diluted with water and, on standing, meconinecarboxylic acid crystallised (14 g. and 3—4 g. from the mother-liquor) from the solution. The substance was recrystallised from benzene or from water. The pure acid (10 g.) (dried in a vacuum at 78°) was covered with dry benzene (20 c.c.), and purified thionyl chloride (20 c.c.) added, the mixture being then gently warmed until evolution of hydrogen chloride appeared to have ceased. The volatile materials were then removed by distillation in a vacuum below 100° and the residue was once more warmed with thionyl chloride (20 c.c.) and isolated in the same manner as before. The crude acid chloride, completely freed from thionyl chloride, was dissolved in benzene (100 c.c.) and gradually added to a dry benzene solution of β-piperonylethylamine (prepared from 20 g. of the hydrochloride). After remaining over-night, the mixture was heated on the steam-bath for 15 minutes, cooled, and filtered. The precipitate was washed with dilute hydrochloric acid, whilst the benzene solution was washed with hydrochloric acid and aqueous sodium carbonate and evaporated. The desired amide, m. p. 148°, was obtained both from the separated solid and from the solution, and after crystallisation from alcohol 9 g. of the pure substance were obtained, whilst 3 g. were subsequently recovered from the alcoholic mother-liquor.

Oxyberberine.—Meconinecarboxy-β-piperonylethylamide (4·5 g.) and freshly distilled phosphoryl chloride (45 c.c.) were heated together on the steam-bath during 5 hours. The mixture was decomposed by means of crushed ice, and the liquid filtered, leaving a small residue (A). The bright yellow filtrate and washings (totalling about 700 c.c.) were rendered faintly alkaline with sodium hydroxide, when an ochre-yellow base was precipitated. The substance was collected, well washed with water, and dried in the air. This base becomes crystalline in contact with alcohol, but some change appears to occur when it is treated with the hot solvent and we have not yet obtained the compound in a pure condition. The entire crude basic product from the experiment described above was mixed with zinc dust (10 g.) and acetic acid (50 c.c.), the mixture boiled during 5 minutes, a second equal portion of zinc dust was then added, and the boiling continued for 25 minutes. The cooled solution was diluted with a relatively large volume of ethyl acetate, filtered, and washed several times with dilute hydrochloric acid,

then with aqueous sodium hydroxide and with water. The solution was dried by means of potassium carbonate, filtered, and the solvent removed by distillation. The yellow, crystalline residue was mixed with alcohol (20 c.c) and after the addition of sodium hydroxide (2 g.) in water (5 c.c.) the whole was heated on the steam-bath during 5 minutes. The flocculent precipitate obtained on the addition of water was now free from the original amide, with which a specimen, obtained in an earlier experiment, was found to be contaminated. The substance was collected, washed, dried at 100° (0·6 g.), and crystallised successively from alcohol, xylene, and alcohol. The woolly needles change in contact with the solvent into rather larger, pale yellow, flat needles, m. p. 198—200° (Found :*N = 4·16. Calc. for $C_{20}H_{17}O_5N$, N = 3·99%). The melting point of oxyberberine given by Perkin (*loc. cit.*, p. 1085) is 198—200°, and this is certainly the value obtained if the substance is submitted to ordinary processes of purification. An exceptionally pure specimen was, however, obtained by crystallisation as the acetate, then as free base from ethyl acetate and alcohol. This product was used in an attempt to reduce the substance by means of zinc dust and hydrochloric acid in alcoholic solution; it was recovered and thrice crystallised from xylene and once from alcohol. The nearly colourless needles melted at 200—201° and a mixture with the synthetical specimen melted at 199—200°. We have also mixed the synthetical material with an ordinary authentic specimen of oxyberberine, m. p. 198—200°, and observed no depression of the melting point. The behaviour of the synthesised material with solvents, its habit of crystallisation, and the form of the crystals, were identical with the corresponding properties of oxyberberine. The bluish-violet fluorescence in neutral organic solvents, which is bright in the light of burning magnesium, was identical with that exhibited by oxyberberine, and the characteristic reaction of the substance with 50% sulphuric acid and a drop of nitric acid (giving an intense violet colour and a permanganate-coloured precipitate on dilution with water) was identical in the case of both specimens. The acetate derived from the synthetical specimen crystallised from acetic acid in hexagonal tablets.

The residue (A) was dissolved in hot glacial acetic acid and, on cooling, a small amount of yellow crystals separated. The substance was several times recrystallised from acetic acid, in which it was sparingly soluble, and obtained as a crust of yellow needles, m. p. 230°, and containing chlorine. The substance shows

* We are indebted to Mr. J. C. Smith, M.Sc., for carrying out this microanalysis by the Pregl-Dumas method.

the characteristic reactions of methyl*nor*oxyberberine * (Faltis, *Monatsh.*, 1910, **31**, 557), m. p. 245°, but it depresses the melting point of this substance when mixed with it and is probably a chloromethyl*nor*oxyberberine derived from dioxyberberine by replacement of a hydroxyl group by a chlorine atom accompanied by demethylation. In the course of our further work we hope to collect sufficient of this substance to enable us to characterise it by analysis.

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[*Received, February 16th*, 1925.]

CIV.—*The Surface Tensions of Aqueous Solutions of Various Organic Compounds.*

By PERCIVAL ROWLAND EDWARDS.

DURING the course of work on adsorption at air-liquid interfaces it became necessary to make determinations of the surface tension of aqueous solutions of different organic compounds. The method proposed by Ferguson (*Trans. Faraday Soc.*, 1921, **16**, 384) was adopted, as apparently the soundest from a theoretical point of view. This method consists in dipping a capillary tube, of known diameter, for some small portion of its length into the liquid whose surface tension is to be determined, and measuring the pressure required to force the liquid down in the capillary tube until the meniscus is flat and just level with the end of the capillary.

The pressure was exerted by raising and lowering a water reservoir and was measured by means of a paraffin manometer, which was read by a cathetometer reading to 0·005 mm. The mean of four pressure readings was taken in each case. The depth at which

* *Correction.*—Having had occasion to prepare methyl*nor*oxyberberine, $C_{19}H_{15}O_5N$, by the method of Faltis (*loc. cit.*), we were struck by its resemblance to the *iso*oxyberberine of Bland, Perkin, and Robinson (J., 1912, **101**, 262) and found, on making a direct comparison, that the substances are indeed identical. The name *iso*oxyberberine has therefore no longer any significance. Careful fresh analyses have confirmed the view of Faltis in regard to the composition of the compound (Found: C = 67·5, 67·8, 67·5; H = 4·6, 4·7, 4·5. $C_{19}H_{15}O_5N$ requires C = 67·6; H = 4·5. $C_{20}H_{17}O_5N$ requires C = 68·4; H = 4·8%). Methyl*nor*oxyberberine is derived from oxyberberine by hydrolysis of one methoxyl group, but we have not found it possible to reconvert the phenol into oxyberberine by vigorous treatment with methyl sulphate and methyl-alcoholic potassium hydroxide (Found, in recovered material: MeO = 8·9. $C_{19}H_{15}O_5N$ containing 1MeO requires MeO = 9·2%). The properties of methyl*nor*oxyberberine and its relation to oxyberberine will be further investigated.—W.H.P., R.R.

the capillary tube was immersed in the liquid was kept constant by means of a pointer, fused to the side of the tip and just touching its own image on the surface of the liquid.

The radius of the capillary tube at its tip and the distance of the pointer from the end of the tube were determined by means of a microscope eyepiece scale, which was calibrated against a Zeiss standard subdivided millimetre scale. The mean of six readings was taken in each case. The radii of the two capillary tubes used were (A) 0·0194 cm. and (B) 0·0225 cm. and the distance of the pointer from the capillary tip was (A) 0·180 cm., (B) 0·120 cm.

The capillary tube, when not in use, was kept in dichromate solution. Prior to use, it was rinsed several times with water, then with alcohol, and finally with water and the solution to be used. The solution was contained in a plane-sided glass cell (5 cm. cube, mounted on a stand with fine screw adjustment). The whole apparatus was placed in a small chamber the temperature of which was constant to within $\pm$ 0·02° during an experiment.

The surface tension of a solution was calculated by means of the expression

$$\gamma = gr/2 \,.\, (\rho_1 h_1 - \rho_2 h_2) + g\rho_2 r^2/6,$$

where r = internal radius of the capillary tube at the tip; h_1 = pressure in cm. of paraffin; ρ_1 = density of the paraffin in g./c.c. = 0·8112 g./c.c. at 16·0°; h_2 = distance between the pointer and the tip = depth of immersion of the tip in the solution; ρ_2 = density of the solution in g./c.c. (in these cases always very nearly unity).

The solutions were made by dissolving weighed quantities of the substances in boiled-out, distilled water and diluting the solutions to 100 c.c. The more dilute solutions of amyl alcohol, menthol, camphor, and thymol in water were made by diluting stronger solutions prepared as described above. The highest concentrations approached the limits of solubility of the substances used.

TABLE I.

Surface tension (γ in dynes per cm.) of aqueous solutions. Concentrations (c) are in g. per 100 c.c. of solution. Tube A.

Merck's pure amyl alcohol redistilled, b. p. 137·8°.

$t°$ ...	15·0	16·0	15·0	16·0	15·0	15·0	15·0	15·0	15·0
c ...	2·000	1·000	1·000	0·500	0·500	0·250	0·250	0·125	0·000
γ ...	35·35	43·68	44·16	53·04	53·14	59·91	59·85	65·38	75·10

The following three, menthol, camphor, and thymol, were studied on account of the well-known peculiar behaviour of their crystals when placed on a water surface.

Menthol (British Drug Houses), m. p. 215·6°.

$t°$	16·0	16·0	16·0	15·0	15·0
c	0·0000	0·0005	0·0011	0·0021	0·0043
γ	75·00	74·76	74·37	72·36	69·34

Camphor (British Drug Houses), m. p. 176·0°.

$t°$	17·0	17·5	17·0	17·0	17·0	16·5
c	0·0000	0·0135	0·0271	0·0542	0·1083	0·2166
γ	74·89	74·59	74·45	73·80	72·74	71·96

Thymol (British Drug Houses), m. p. 49·7°.

$t°$	17·5	17·5	17·5	18·0	18·0	18·0
c	0·0000	0·0034	0·0068	0·0125	0·0250	0·0500
γ	74·81	73·61	71·51	67·53	61·80	55·54

It is evident, therefore, that the " dancing " of these substances, familiar in the case of camphor when placed on the surface of water, is due to the lowering of the surface tension. A crystal of *p*-toluidine " dances " more vigorously than any of the above.

The surface tensions of aqueous solutions of the following substances also were measured.

TABLE II.

Surface Tension of Aqueous Solutions of Various Organic Compounds.

Substance.	Source.	Tube.	Temp.	c.	γ.
Phenacetin	B.D.H.	A	16·0°	0·1080	72·81
Camphoric acid	,,	,,	,,	0·5852	57·33
		,,	,,	0·6500	55·69
		,,	,,	0·6500	56·04
Aceto-*p*-toluidide	,,	,,	,,	0·1000	72·48
		,,	17·0	0·1000	72·18
Piperonal	,,	,,	,,	0·1600	72·83
		B *	,,	0·1600	72·83
Hippuric acid	,,	A	16·5	0·3000	74·27
		B	,,	0·3000	74·53
Ethyl succinate	Merck	,,	18·0	1·5966	48·11
Methyl salicylate	,,	,,	16·0	0·3600	67·18
Ethyl malonate	Kahlbaum	,,	17·0	1·9636	49·53
Salicylic acid	,,	,,	14·5	0·1400	71·41

* Tube B gave $\gamma = 75·09$ and $\gamma = 74·88$ for water at 15·0° and 17·0°, respectively.

A series of accurate determinations was also carried out with solutions of well recrystallised *p*-toluidine (Kahlbaum, m. p. 45·6°; solubility 0·654 g. in 100 c.c. of water at 15·0°).

Each surface tension reading was obtained by taking the mean of six pressure readings.

The form of the surface tension–concentration curves is highly individual; *e.g.*, that for *p*-toluidine, showing a point of inflection, is in striking contrast to that for amyl alcohol. In all cases, however, the surface tension tends to approach a constant value,

TABLE III.

Surface Tensions of Aqueous Solutions of p-*Toluidine.*

Tube.	Temp.	*c.*	γ.	Tube.	Temp.	*c.*	γ.
A	17·0°	0·0000	74·90	A	16·0°	0·1300	65·98
,,	,,	0·0000	74·83	B	,,	0·1500	65·14
B	16·0	0·0200	74·50	A	16·5	0·1600	62·65
A	,,	0·0300	74·44	,,	16·0	0·1800	61·31
,,	,,	0·0600	73·33	,,	16·5	0·2250	58·22
,,	,,	0·0600	73·31	,,	16·0	0·3000	54·43
B	17·0	0·0700	73·13	,,	17·5	0·3000	53·27
A	,,	0·0800	71·97	,,	15·5	0·3000	54·61
,,	,,	0·1000	69·63	,,	16·0	0·3600	50·15
,,	16·5	0·1000	69·67	,, *	,,	0·4500	47·41 *
B	15·0	0·1100	69·39	,, *	17·0	0·6000	42·31 *
A	16·0	0·1200	67·57	,, *	,,	0·6000	42·44 *

* In almost saturated solutions it became difficult to obtain accurate readings owing to excessive "stickiness" and "foaming."

although this is not attained even in saturated solution.* Although all the substances are crystalloids, the lowering of the surface tension is comparable with that of the most active colloids.

A number of other substances, such as phenyldimethylcarbamide, phenylacetanilide, erucic acid, salol, *p*-cresol, and *iso*amyl valerate, were investigated, but owing to their very low solubility in water, quantitative readings were not taken. The last-named substance remains on a water surface in the form of droplets which "dance" in a similar manner to camphor.

In all cases the relative lowering of the surface tension of water by these organic compounds can be readily explained on the basis of the Harkins-Langmuir theory of "polar" molecules and surface tension.

In conclusion, the author wishes to thank Prof. McBain, at whose suggestion the work was carried out, for helpful advice, and the Chemical Society for a grant for materials.

THE UNIVERSITY, BRISTOL. [*Received, January 21st*, 1925.]

* If, as seems possible, the surface layer of a solution containing a very readily adsorbed substance always becomes covered with a monomolecular film of solute when saturation concentration is approached, the surface tension should approach a constant value in each case. This would explain the tendency of surface-tension curves to become parallel to the concentration axis as saturation is approached. With a view to test this conclusion, Mr. G. P. Davies has made measurements with a Du Nouy tensimeter. At least 15 secs. were allowed for the surfaces to age. For water and solutions containing 0·45, 0·60, and 0·65 g., respectively, of *p*-toluidine the surface tensions found were 73·2, 53·7, 51·4, and 51·8 dynes per cm. These results support the suggestion here put forward.

CV.—*Quantitative Reduction by Hydriodic Acid of Halogenated Malonyl Derivatives. Part IV. The Influence of Substitution in the Amide Group on the Reactivity of the Halogen Atom in Bromomalonamide.*

By RALPH WINTON WEST.

IN Part II of this series (J., 1922, **121**, 2196), it was shown that substitution in the amide groups of malonamide markedly affects the ease of halogenation of the malonyl methylene group, steric rather than polarity factors being the determining influence. In the investigation of such a problem, however, it is essential to consider not only the ease of introduction of the halogen atom, but also the ease of its removal. By the estimation of the velocity coefficient of the reaction $\text{:CHBr} + \text{HI} = \text{:CH}_2 + \text{IBr}$, already discussed (J., 1924, **125**, 710), it has been possible to study the effect of the presence of some commonly occurring groups on the reactivity of the bromine atom. In order thoroughly to test the effects of the groups, the compounds were as far as possible considered in sets of three, (I) R'·CO·CHBr·COR', (II) R''CO·CHBr·COR'', (III) R'CO·CHBr·COR'', such that III is the compound intermediate between I and II.

Velocity coefficients at 25°.

R'.	R''.	k_1.	k_2.	k_3.	Calc. k_3.
NH_2	NHEt	0·81	1·12	0·93	0·87
,,	$NHPr^{\beta}$	,,	1·50	0·95	1·00
,,	NH·C_4H_9 (*iso*)	,,	1·60	1·12	1·03
,,	NH·C_6H_4Me (*p*)	,,	17·5	3·15	3·21
NHMe	,,	1·01	,,	3·99	3·91
NHEt	,,	1·12	,,	4·34	4·29
$NHPr^{\beta}$	,,	1·50	,,	5·57	5·58
NH·C_4H_9 (*iso*)	,,	1·60	,,	5·87	5·92
NH·CH_2Ph	,,	(1·63)	,,	6·04	—
OH	,,	—	,,	9·6	—
OEt	,,	—	,,	13·3	—
NHEt	$NHPr^{\beta}$	1·12	1·50	1·42	1·34
NH_2	NH·C_6H_4Br (*p*)	0·81	(80)	6·61	—
NHMe	,,	1·01	(79)	8·0	—
NHEt	,,	1·12	(85)	9·11	—

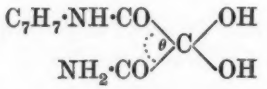
The figures given in the column headed k_3 (calc.) are obtained by means of the formula $\log k_3 = 0{\cdot}9 \log k_1 + 0{\cdot}474 \log k_2$, where $k_2 > k_1$. This formula is empirical, but gives results in good agreement with those found by experiment, suggesting that, although the mathematical basis of the problem is not understood, yet it should be relatively simple in character. The figures in brackets also are calculated, experimental difficulties making direct estim-

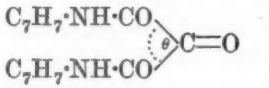
ation impossible. The three values so obtained for bromomalon-*p*-bromoanilide are in fair agreement with one another, but are probably too high, as the figure is outside the range of the experimental expression.

From this table it is possible to arrange the groups in ascending order of their effect on the reactivity of the bromine atom:

NH_2, NHMe, NHEt, $NHPr^{\beta}$, $NH{\cdot}C_4H_9(iso)$, $NH{\cdot}CH_2Ph$, OH, OEt, $NH{\cdot}C_6H_4Me(p)$, $NH{\cdot}C_6H_4Br(p)$.

By an extension of the steric explanation of Chattaway and Harrison (J., 1916, **109**, 172), whereby an increase in the groups R′ and R″ would tend to decrease the solid angle occupied by the bromine atom and so increase its reactivity, the order of the groups could be explained with the exceptions of OH and OEt, which are too high in the series. As, in considering steric relationships, the configuration of the groups must be taken into account in addition to their additive molecular volumes, it is possible to conceive that *iso*butyl and benzyl have very similar steric volumes. The sudden rise, however, in the case of *p*-tolyl requires explanation.

(IV.) 

 (V.)

Plowman and Whiteley (J., 1924, **125**, 587) have shown that mesoxmono-*p*-tolylamide is more stable in the dihydroxy-form (IV), and that mesox-*p*-toluidide is more stable in the keto-form (V). Having regard to the fact that mesoxalic ester exists in the dihydroxy-form, it is necessary to base the explanation on steric factors, and not on polarity effects. The authors suggest that the increase in θ in passing from (IV) to (V) would cause congestion of the hydroxy-groups and a tendency to form a stable double linking. In the closely related bromomalonyl compounds it would be expected to follow that the steric effects of the para-substituted phenyl groups would be correspondingly large.

From the polarity theory put forward by Lapworth (*Mem. Manchester Phil. Soc.*, 1920, **64**, ii, 10), and the electronic theory of J. J. Thomson (*Phil. Mag.*, 1923, [vi], **46**, 497), it would be expected that OH and OEt would bring about the greatest increase in the reactivity of the bromine atom. This might account for the high position of these groups in the sequence, but it is only one of several directions in which an explanation of the relative effects of the OX and NHX groups is to be sought.

Thus it would appear that the influence of a group on the reactivity of the halogen atom in this series of compounds is some function of the electronic and steric effects of the group.

Some of the velocity coefficients were also measured at 30·2°. The results are readily correlated by an empirical expression similar to that used for the results at 25°, *viz.*, $\log k_3 = 0{\cdot}7 \log k_1 + 0{\cdot}522 \log k_2$. The variation of the temperature coefficients suggests that the reaction proceeds in several stages, each of which is controlled by a separate energy equation.

Experimental.

Malondiisopropylamide.—A mixture of ethyl malonate (9·5 g.) and *iso*propylamine (7 g.) was heated in a sealed tube at 120° for 2 hours and at 160° for 7 hours. The alcohol was removed and the solid crystallised from petroleum, separating in needles (9 g.), m. p. 114° (Found: N = 15·13. $C_9H_{18}O_2N_2$ requires N = 15·07%).

Malonmonoethylamide.—Ethyl malonamate (5 g.) was mixed with excess of monoethylamine solution, and kept for 24 hours. After evaporation to dryness, the product separated from alcohol-benzene in plates (4·5 g.), m. p. 123° (Found: N = 21·65. $C_5H_{10}O_2N_2$ requires N = 21·54%).

Malonmonoisopropylamide.—A mixture of ethyl malon*iso*propylamate and excess of ammonia solution was kept for 48 hours. After evaporation, the product separated from alcohol–benzene in prisms, m. p. 129° (Found: N = 19·60. $C_6H_{12}O_2N_2$ requires N = 19·44%).

Malonmonoisobutylamide.—A mixture of ethyl malonate (12 g.) and *iso*butylamine (5 g.) was heated in a sealed tube for 24 hours at 100°. The alcohol was removed on the water-bath, the resulting deliquescent solid allowed to absorb moisture, and the malondi-*iso*butylamide filtered off. The filtrate was mixed with excess of ammonia solution, and kept for 24 hours. The solid obtained on evaporation was dissolved in 5 c.c. of alcohol, the solution well cooled, and the malonamide filtered off. The *malonmonoisobutylamide* obtained on evaporation separated from benzene in needles, m. p. 83° (Found: N = 17·81. $C_7H_{14}O_2N_2$ requires N = 17·72%).

Malonmonoethylmonoisopropylamide, $NHEt{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}NHPr^s$, obtained by condensing ethyl malon*iso*propylamate with monoethylamine, separated from petroleum in needles, m. p. 98° (Found: N = 16·21. $C_8H_{16}O_2N_2$ requires N = 16·29%).

Malonmonomethylmonophenylamide, m. p. 151° (Found: N = 14·50. $C_{10}H_{12}O_2N_2$ requires N = 14·58%), and *malonmonoethylmonophenylamide*, m. p. 154° (Found: N = 13·71. $C_{11}H_{14}O_2N_2$ requires N = 13·59%), were each prepared by allowing ethyl malonanilate to stand in contact with a solution of the corresponding amine for 24 hours. In each case, the product was extracted with

boiling water, the required product separating from the solution on cooling.

Malonmonomethylmono-p-*tolylamide*, m. p. 183° (Found : N = 13·70. $C_{11}H_{14}O_2N_2$ requires N = 13·59%), and *malonmonoethylmono*-p-*tolylamide*, m. p. 176° (Found : N = 12·68. $C_{12}H_{16}O_2N_2$ requires N = 12·73%), were prepared similarly to the corresponding phenyl compounds, and separated from water in plates.

*Malonmonoiso**propylmono*-p-*tolylamide*, m. p. 192° (Found : N = 11·90. $C_{13}H_{18}O_2N_2$ requires N = 11·97%), *malonmonoiso**butylmono*-p-*tolylamide*, m. p. 177° (Found : N = 11·39. $C_{14}H_{20}O_2N_2$ requires N = 11·29%), and *malonmonobenzylmono*-p-*tolylamide*, m. p. 188° (Found : N = 10·07. $C_{17}H_{18}O_2N_2$ requires N = 9·93%), were each prepared by heating ethyl malon-*p*-toluidate with the corresponding amine in a sealed tube at 120° for 4½ hours. They separate from alcoholic solution in needles.

Bromination of the Substituted Malonamides. General Methods.—(1) For those compounds containing the phenyl group, the general formula for the brominated product being

$$R{\cdot}NH{\cdot}CO{\cdot}CHBr{\cdot}CO{\cdot}NH{\cdot}C_6H_4Br(p).$$

The amide (1 mol.), dissolved in hot acetic acid, was slowly treated with a solution of bromine (2 mols.) in the same solvent. The solvent was removed at the room temperature, the product treated with a small quantity of ether, and filtered.

(2) For compounds not containing the phenyl group, the general formula for the brominated product being

$$R'{\cdot}NH{\cdot}CO{\cdot}CHBr{\cdot}CO{\cdot}NHR''.$$

The procedure was as described in (1), except that one mol. of bromine was used. Several of the compounds yielded syrups, but these were readily rendered solid by repeated treatment with small quantities of petroleum (b. p. 40—60°).

*Bromomalondiiso**propylamide*, m. p. 204° (Found : Br = 30·02. $C_9H_{17}O_2N_2Br$ requires Br = 30·16%), *bromomalonmonomethylmono*-p-*bromophenylamide*, m. p. 187° [Found : Br (malonyl) = 22·56. $C_{10}H_{10}O_2N_2Br_2$ requires Br (malonyl) = 22·85%], *bromomalonmonomethylmono*-p-*tolylamide*, m. p. 186° (Found : Br = 27·90. $C_{11}H_{13}O_2N_2Br$ requires Br = 28·07%), *bromomalonmonoethylmono*-p-*tolylamide*, m. p. 178° (Found : Br = 26·60. $C_{12}H_{15}O_2N_2Br$ requires Br = 26·73%), and *bromomalonmonobenzylmono*-p-*tolylamide*, m. p. 167° (Found : Br = 22·02. $C_{17}H_{17}O_2N_2Br$ requires Br = 22·14%), all separate from alcohol in needles. *Bromomalonmonoethylamide*, m. p. 161° (Found : Br = 38·41. $C_5H_9O_2N_2Br$ requires Br = 38·23%), and *bromomalonmonoiso**butylamide*, m. p. 156° (Found : Br = 33·64. $C_7H_{13}O_2N_2Br$ requires Br = 33·72%), separate from alcohol–benzene in needles. *Bromomalonmonoethyl-*

mono-p-*bromophenylamide*, m. p. 179° [Found: Br (malonyl) = 22·08. $C_{11}H_{12}O_2N_2Br_2$ requires Br (malonyl) = 21·98%], *bromomalonmonoisopropylmono*-p-*tolylamide*, m. p. 179° (Found: Br = 25·31. $C_{13}H_{17}O_2N_2Br$ requires Br = 25·54%), and *bromomalonmonoisobutylmono*-p-*tolylamide*, m. p. 148° (Found: Br = 24·56. $C_{14}H_{19}O_2N_2Br$ requires Br = 24·44%), separate from dilute alcohol in needles. *Bromomalonmonoisopropylamide*, m. p. 192° (Found: Br = 35·60. $C_6H_{11}O_2N_2Br$ requires Br = 35·83%), *bromomalonmonoethylmonoisopropylamide*, m. p. 172° (Found: Br = 31·71. $C_8H_{15}O_2N_2Br$ requires Br = 31·84%), and *bromomalonmono*-p-*tolylamide*, m. p. 202° (Found: Br = 29·50. $C_{10}H_{11}O_2N_2Br$ requires Br = 29·48%), separate from ethyl acetate, benzene, or acetic acid–water in needles.

Bromomalon-p-*toluidide*.—The substance described (J., 1921, **119**, 359) as melting at 211° would not give a regular velocity coefficient, and proved to be a constant-crystallising mixture of the dibromo- and unchanged compounds.

Malon-*p*-toluidide (5 g.), dissolved in 300 c.c. of boiling acetic acid, was slowly treated with 10 c.c. of a 10% solution of bromine in the same solvent. Throughout the addition (20 minutes) the solution was vigorously shaken, and maintained at the boiling point. On cooling, the pure bromomalon-*p*-toluidide crystallised. It separated from acetic acid in plates, m. p. 217° (Found: Br = 22·00. $C_{17}H_{17}O_2N_2Br$ requires Br = 22·14%).

Velocity Measurements.

Methyl alcohol containing 4% of water and 2% of acetic acid (by volume) was an excellent solvent for the substances under investigation, concordant readings being obtained with the minimum of interference from side reactions. The methyl alcohol was treated with alkaline hypoiodite to remove acetone, dried, and distilled. The acetic acid was of the quality already described (J., 1921, **119**, 364). The quantity of potassium iodide used was that required by the equations:

a. . . . $:CHBr + HI = :CH_2 + IBr$ (measured reaction)
b. . . . $IBr + HI = I_2 + HBr$ (instantaneous reaction)

The calculations were therefore based on the expression $dx/dt = k'(a - x)(2a - 2x)$, which gives on integration, $k = 2k' = x/at(a - x)$. For convenience, the values of k are given in the tables and not those of k'.

Owing to the rapidity of some of the reactions, the experimental error is greater than is usual in such determinations.

Determination of the Velocity Coefficients.

R'.	R''.	Temp. 25°. No. of deterns.	Limits of k.	Mean.	Temp. 30·2°. No. of deterns.	Limits of k.	Mean.	$k_{30\cdot2°}/k_{25°}$
NH_2	NH_2	7 *	0·79—0·82	0·81	6 *	1·11—1·15	1·14	1·41
NH_2	$NHEt$	6 *	0·91—0·93	0·93	6 *	1·41—1·45	1·43	1·54
NH_2	$NHPr^{\beta}$	6	0·92—0·97	0·95	7 *	1·44—1·51	1·47	1·55
NHMe	NHMe	8 *	0·98—1·04	1·01	7 *	1·59—1·69	1·64	1·62
NHEt	NHEt	8 *	1·07—1·15	1·12	6 *	1·78—1·87	1·83	1·63
NH_2	$NH{\cdot}C_4H_9$ (*iso*)	7	1·10—1·14	1·12				
NHEt	$NHPr^{\beta}$	4	1·41—1·44	1·42				
$NHPr^{\beta}$	$NHPr^{\beta}$	7 *	1·45—1·54	1·50	7 *	2·14—2·28	2·19	1·46
$NH{\cdot}C_4H_9$ (*iso*)	$NH{\cdot}C_4H_9$ (*iso*)	6 *	1·56—1·64	1·60	6 *	2·67—2·82	2·75	1·72
NH_2	$NH{\cdot}C_6H_4Me$ (*p*)	8 *	3·12—3·21	3·15	6 *	5·30—5·38	5·33	1·69
NHMe	,,	7	3·94—4·05	3·99	5 *	6·98—7·17	7·06	1·77
NHEt	,,	7	4·25—4·45	4·34	6 *	7·71—7·86	7·78	1·79
$NHPr^{\beta}$	,,	6	5·42—5·71	5·57	8	8·14—8·54	8·34	1·50
$NH{\cdot}C_4H_9$ (*iso*)	,,	7	5·81—6·04	5·91	8	8·43—9·11	8·77	1·49
$NH{\cdot}CH_2Ph$	,,	7	5·99—6·09	6·04	7	8·66—9·02	8·85	1·46
NH_2	$NH{\cdot}C_6H_4Br$ (*p*)	6	6·50—6·75	6·61	6 *	10·6—11·3	11·0	1·66
NHMe	,,	6	7·80—8·12	8·0				
NHEt	,,	6	8·89—9·25	9·11				
OH	$NH{\cdot}C_6H_4Me$ (*p*)	3	9·2—10·2	9·6				
OEt	,,	6	13·0—13·7	13·3				
$NH{\cdot}C_6H_4Me$ (*p*)	,,	7	16·8—18·7	17·5	5	19·5—20·8	20·2	1·14

* In these experiments, initial concentration of bromo-compound = 0·008614 g.-mol./litre.
In other ,, ,, ,, ,, ,, ,, = 0·004307 ,,

In conclusion, the author desires to express his thanks to the Chemical Society for a grant from the Research Fund, and to Assistant-Professor M. A. Whiteley for the interest taken in the progress of this research.

IMPERIAL COLLEGE, S.W. 7. [*Received, January 15th*, 1925.]

CVI.—*The Velocity of Reaction in Mixed Solvents. Part VIII. The Velocity of Formation of certain Quaternary Ammonium Salts.*

By HAMILTON MCCOMBIE, HUGH MEDWYN ROBERTS, and HAROLD ARCHIBALD SCARBOROUGH.

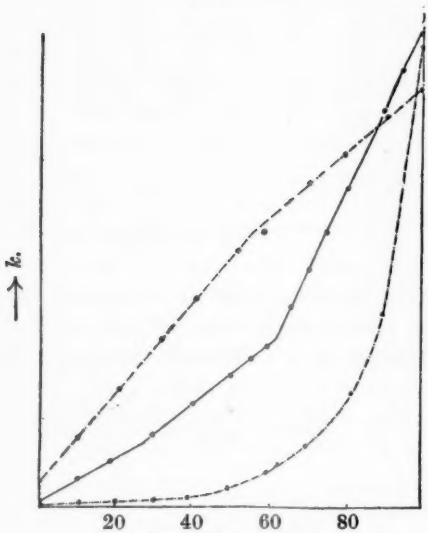
IN a previous communication (J., 1923, **123**, 1229), the velocity of formation of certain quaternary ammonium salts in mixed solvents was studied; and it was suggested that, if the curve showing the relation between k and the percentage composition of the solvent were divisible into linear sections, it would seem that not only had a solvent complex been formed, but also that this complex underwent further complex formation with one of the reactants or reaction products.

In order to obtain further information the velocity of formation of quaternary ammonium salts has been studied in different solvent pairs.

The Addition of Allyl Bromide to Pyridine in Benzene–Nitrobenzene Mixtures.

This reaction was studied by Hawkins (J., 1922, **121**, 1179); and it was shown that the existence of a complex between the solvent and a reactant was not to be expected. The velocity of formation of the quaternary ammonium salt was studied in nitrobenzene–benzene mixtures at 30°; the experimental results are shown in Tables I and II. The curve (Fig. 1) was found to be divisible into three linear sections which would intersect at the compositions 61·2 and 27·4% of nitrobenzene. Such compositions agree closely with those demanded by the complexes $C_6H_5{\cdot}NO_2,C_6H_6$ and $4C_6H_6,C_6H_5{\cdot}NO_2$, respectively.

FIG. 1.



— · — · — p-*Nitrobenzyl chloride and trimethylamine in* n-*hexane–*α-*bromonaphthalene mixtures.*
———— *Allyl bromide and pyridine in benzene–nitrobenzene mixtures.*
– – – – – ω-*Bromoacetophenone and pyridine in benzene–acetone mixtures.*

These results correspond with those obtained in the case of the reaction between trimethylamine and *p*-nitrobenzyl chloride (*loc. cit.*).

An examination of the physical constants for benzene–nitrobenzene mixtures showed that the only evidence of complex formation is the occurrence of a maximum in the viscosity curve at 62% of nitrobenzene (*Amer. J. Sci.*, 1896, [iv], **2**, 336).

The refractive index of benzene–nitrobenzene mixtures at 15° for the D line has been determined; the results are given in Table III. The curve is slightly bowed, but shows no marked change in direction.

A most noticeable point about this reaction was the form in which the quaternary ammonium salt was precipitated. In only one solvent composition—60% of nitrobenzene—did it appear to be a solid; in mixtures containing 55 and 65% of nitrobenzene the precipitate was semi-solid, and at all other compositions of the solvent it appeared as a dark red oil. That this change in the

appearance of the ammonium salt should occur at the point of inflection may have no significance, yet it does serve to illustrate our view that, although a curve may be divisible into linear sections, it does not follow that a sudden change occurs at the point of inflection; but rather that this change is occurring over a range of solvent composition. The point of inflection is the point at which the maximum effect is produced and any change in the direction of the curve must be supposed to originate at this point.

The Addition of ω-Bromoacetophenone to Pyridine in Benzene–Acetone Mixtures.

This reaction has been studied by Clarke (J., 1910, **97**, 416) in alcoholic solution at 55·6°. The velocity of formation of the ammonium salt was measured in benzene–acetone mixtures at 30°; the experimental results are shown in Tables V and VI. The curve (Fig. 1) appears to be divisible into two linear sections which would intersect at 55% of acetone. Such a composition would agree with the complex $2C_3H_6O,C_6H_6$, which requires 54·6% of acetone. It is to be noted that the value of k in 60% acetone lies away from either section of the curve and thus tends to emphasise the fact that the curve consists of two linear sections. It is felt, however, that this coincidence must not be stressed, as the difference between the values of k in two consecutive solvent mixtures is only about three or four times the experimental error. The general shape of the curve is worthy of note. The reaction proceeds in pure acetone about 18 times as fast as in pure benzene; as the percentage of benzene in the solvent is increased, the value of k falls slowly but is always greater than the value of k calculated on the assumption that k will lie on a straight line joining the values in the pure solvents.

In all cases previously studied, the addition of that solvent in which the reaction proceeds more slowly causes a large decrease in the value of k. If in the case of the acetone–benzene mixtures a straight line be drawn joining the values of k in the two pure solvents, the maximum deviation of the curve from this straight line is equivalent to only about 20% in the value of k. In all other cases considered, this deviation would be equivalent to anything between 100 and 1000%.

The Addition of p-*Nitrobenzyl Chloride to Trimethylamine in* n-*Hexane–*α*-Bromonaphthalene Mixtures.*

The velocity of addition of *p*-nitrobenzyl chloride to trimethylamine has been measured by von Halban (*Z. physikal. Chem.*, 1913, **84**, 129) in solvents of widely differing chemical character.

It was found that, at 30°, the time for half the reaction to be completed in *n*-hexane was some 80 days and but some 4 hours in α-bromonaphthalene solution. The difference in reaction velocity is so great, in these two solvents, that it is comparable with the velocity of saponification of esters in alcohol–water mixtures. The use of such an inert solvent as *n*-hexane might be expected to exclude the possibility of complex formation between the solvents; thus the curve would represent a reaction proceeding in substances which play no *rôle* but that of solvent. The experimental results are shown in Tables VIII and IX; the curve (Fig. 1) is smooth and not divisible into linear sections.

A comparison of this reaction with the reaction studied in benzene–acetone mixtures shows the marked difference brought about by the addition of that solvent in which the reaction velocity is small. The first addition of *n*-hexane lowers the value of k to about 45% of the value of k in pure α-bromonaphthalene; for each additional 10% of *n*-hexane the constant is approximately halved. The maximum deviation of k from the value of k calculated on the assumption that a linear relationship holds is approximately 2200% and the deviation is negative.

EXPERIMENTAL.

The benzene and nitrobenzene were prepared and purified in the manner previously described; the *n*-hexane, α-bromonaphthalene, and acetone (B.D.H. products) were subjected to one fractional distillation. The densities of the benzene–acetone and the *n*-hexane–α-bromonaphthalene mixtures, recorded in Tables IV and VII respectively, were determined in the manner previously described (J., 1923, **123**, 1229).

The pyridine (Kahlbaum) was fractionally distilled, the portion boiling at 116° being retained; the allyl bromide was similarly treated and the portion used boiled at 70·5°. The *p*-nitrobenzyl chloride (m. p. 71°) and the ω-bromoacetophenone (m. p. 51°) were prepared by the usual methods.

The solutions of the reactants were prepared by direct weighing, except in the case of the trimethylamine, the concentration of which was determined by titration. The velocity measurements were made at 30° ± 0·1°. The reactants were contained in sealed tubes; some 10 or 11 tubes were employed for each determination. The filling, draining, and sealing of the tubes were carried out with the tube partly immersed in ice-water. The zero time was taken as that moment at which the tube was placed in the thermostat. The progress of the reaction was followed by titrating the ionic halogen according to Volhard's method.

The velocity coefficient was calculated from either the equation :

$$k = 2{\cdot}302/(a - b)t \,.\, \{\log (a - x)/(b - x) \,.\, b/a\} \quad . \quad . \quad . \quad (1)$$

or

$$k = x/t\sqrt{ab(a - x)(b - x)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where a and b are the initial concentrations in g.-mol. per litre and t is the time in minutes. Equation 2 was used in those cases in which a and b were nearly the same.

Representative results are shown in Tables II, VI, and IX.

The refractive indices recorded in Table III were determined at 15° with a Pulfrich refractometer.

Table I.

Nitrobenzene–Benzene Mixtures at 30°.

Nitrobenzene %.	$c_{pyridine}$ (g.-mol./litre).	$c_{bromide}$ (g.-mol./litre).	Limit k.	k.
100	0·3504	0·3493	0·0147 —0·0151	0·0150
95	0·3503	0·3509	0·0138 —0·0145	0·0139
90·2	0·3504	0·3494	0·0122 —0·0128	0·0126
84·8	0·3531	0·3500	0·0108 —0·0112	0·0110
80	0·3500	0·3515	0·0102 —0·0105	0·0103
74·7	0·3510	0·3524	0·0085 —0·0089	0·0086
70	0·3517	0·3500	0·0069 —0·0071	0·00705
65·1	0·3520	0·3495	0·0061 —0·0064	0·00615
60	0·3515	0·3493	0·0049 —0·0053	0·00505
54·7	0·3525	0·3509	0·0044 —0·0046	0·00455
50·2	0·3501	0·3515	0·0039 —0·0042	0·00405
39·7	0·3526	0·3515	0·00305—0·00315	0·0031
29·9	0·3506	0·3510	0·00205—0·00220	0·00215
19·6	0·3500	0·3512	0·00132—0·00136	0·00135
10	0·3535	0·3520	0·00078—0·00081	0·00080
0	0·3507	0·3947	0·00032—0·00034	0·0003

Table II.

Nitrobenzene–Benzene Mixtures at 30°.

84·8% of Nitrobenzene. $c_{amine} = 0{\cdot}3531$. $c_{bromide} = 0{\cdot}3500$ (g.-mol./litre).			19·6% of Nitrobenzene. $c_{amine} = 0{\cdot}3500$. $c_{bromide} = 0{\cdot}3512$ (g.-mol./litre).		
Time (mins.).	x.	k.	Time (mins.).	x.	k.
32	0·0381	0·0108	363	0·0528	0·00136
108	0·1012	0·0107	1046	0·1135	0·00132
146	0·1269	0·0110	1413	0·1391	0·00133
178	0·1440	0·0111	1780	0·1594	0·00134
207	0·1568	0·0110	2468	0·1886	0·00135
236	0·1680	0·0110	2921	0·2036	0·00136
262	0·1764	0·0110	3209	0·2120	0·00136
319	0·1960	0·0112	3914	0·2255	0·00134
347	0·2017	0·0110	4355	0·2350	0·00134

TABLE III.

Refractive Indices of Benzene–Nitrobenzene Mixtures at 15°.

Nitrobenzene %	100	95	90·2	84·85	81·1	74·75
$n_D^{15°}$	1·55415	1·55130	1·54767	1·54351	1·54150	1·53791
Nitrobenzene %	69·6	65·15	62·13	59·05	54·7	39·7
$n_D^{15°}$	1·53493	1·53262	1·53104	1·52948	1·52734	1·52028
Nitrobenzene %	28·85	19·65	10	0		
$n_D^{15°}$	1·51588	1·51171	1·50785	1·50403		

TABLE IV.

Density of Acetone–Benzene Mixtures at 15°.

Acetone %	100	89·95	80·16	69·47	60·29	49·69
$d_{4°}^{15°}$	0·79769	0·805607	0·81370	0·82272	0·83020	0·83938
Acetone %	40·29	29·72	20·09	9·94	0	
$d_{4°}^{15°}$	0·84768	0·85680	0·86556	0·87490	0·88453	

TABLE V.

Benzene–Acetone Mixtures at 30°.

Acetone %.	$c_{pyridine}$ (g.-mol./litre).	$c_{bromoacetophenone}$ (g.-mol./litre).	Limit k.	k.
100	0·0498	0·0508	0·0860—0·0880	0·0875
90·65	0·0499	0·0504	0·083 —0·084	0·0835
79·85	0·0691	0·0666	0·073 —0·076	0·0755
70	0·0691	0·0666	0·067 —0·070	0·069
59·95	0·0686	0·0663	0·0585—0·0605	0·0595
49·5	0·0679	0·0662	0·0535—0·055	0·054
40	0·0681	0·0661	0·042 —0·047	0·044
29·25	0·0673	0·0664	0·033 —0·0365	0·034
20·10	0·0681	0·0663	0·0245—0·026	0·025
10	0·0685	0·0678	0·014 —0·015	0·0145
0	0·0683	0·0661	0·0046—0·005	0·0048

TABLE VI.

Benzene–Acetone Mixtures at 30°.

79·85% of Acetone. $c_{pyridine} = 0·0671$. $c_{bromoacetophenone} = 0·0656$ (g.-mol./litre).			20·10% of Acetone. $c_{pyridine} = 0·0681$. $c_{bromoacetophenone} = 0·0663$ (g.-mol./litre).		
Time (mins.).	x.	k.	Time (mins.).	x.	k.
76	0·0183	0·0758	253	0·0203	0·0252
176	0·0312	0·0755	430	0·0286	0·0256
204	0·0337	0·0760	901	0·0406	0·0253
244	0·0366	0·0759	1021	0·0426	0·0255
283	0·0389	0·0754	1112	0·0442	0·0258
318	0·0407	0·0752	1250	0·0456	0·0252
338	0·0416	0·0756	1297	0·0461	0·0251
371	0·0431	0·0753	1407	0·0469	0·0244
412	0·0443	0·0735			

Table VII.

α-Bromonaphthalene–*n*-Hexane Mixtures at 15°.

α-$C_{10}H_7Br$ %	100	90	79·9	70	59·9	49·75
$d_{4°}^{15°}$	1·47682	1·33641	1·21802	1·11572	1·02959	0·95566
α-$C_{10}H_7Br$ %	40·1	29·85	19·95	10·1	0	
$d_{4°}^{15°}$	0·89003	0·83120	0·78155	0·73521	0·69411	

Table VIII.

α-Bromonaphthalene–*n*-Hexane Mixtures at 30°.

$C_{10}H_7Br$ %.	c_{amine} (g.-mol./litre).	$c_{chloride}$ (g.-mol./litre).	Limit *k*.	*k*.
100	0·1778	0·1068	0·0172 —0·0177	0·0175
90	0·1583	0·1075	0·0073 —0·0079	0·0075
79·9	0·1769	0·0997	0·0033 —0·0038	0·0036
70	0·1272	0·1010	0·00195 —0·00205	0·00203
59·9	0·2073	0·0666	0·00120 —0·00126	0·00123
49·75	0·1345	0·0703	0·00071 —0·00073	0·00072
40·1	0·1285	0·0458	0·00036 —0·00042	0·00040
29·85	0·1302	0·0454	0·00022 —0·000245	0·00023
19·95	0·1251	0·0386	0·000135—0·00016	0·00015
10·1	0·1373	0·0485	0·000097—0·00011	0·000105
0	0·1262	0·0403	0·000076—0·000080	0·000078

Table IX.

α-Bromonaphthalene–*n*-Hexane Mixtures at 30°.

100% of α-Bromonaphthalene.

c_{amine} = 0·1778. $c_{chloride}$ = 0·1068 (g.-mol./litre).

Time (mins.).	*x*.	*k*.
92	0·0245	0·0172
154	0·0354	0·0172
193	0·0436	0·0177
232	0·0491	0·0177
276	0·0541	0·0175
349	0·0614	0·0175
384	0·0651	0·0177
404	0·0655	0·0172

29·85% of α-Bromonaphthalene.

c_{amine} = 0·1302. $c_{chloride}$ = 0·0454 (g.-mol./litre).

Time (mins.).	*x*.	*k*.
4,320	0·0055	0·000234
8,835	0·0092	0·000223
12,983	0·0137	0·000224
18,730	0·0191	0·000227
34,758	0·0315	0·000224
60,466	0·0365	0·000245
51,775	0·0344	0·000244
79,090	0·0384	0·000221

The authors beg to express their thanks to the Government Grant Committee of the Royal Society for funds placed at their disposal which have defrayed the cost of the research.

The Chemical Laboratories,
Cambridge.

[*Received, December 23rd*, 1924.]

CVII.—*A New Method of Flame Analysis.*

By Oliver Coligny de Champfleur Ellis and Henry Robinson.

In the course of an investigation of the phenomena immediately attendant on the ignition of an inflammable gaseous mixture, the authors have been under the necessity of obtaining instantaneous photographs of the flame-front at very small and accurately known intervals of time after ignition. The revolving-film method of photography, first used by Mallard and Le Chatelier (*Ann. Mines*, 1883, [viii], **4**, 312) for studying the propagation of flame in tubes, normally yields only a time–distance curve with respect to the flame as a whole; it cannot register, for example, the shape of the flame-front at any given stage in the propagation. Mason and Wheeler's modification of the method (J., 1920, **117**, 1233) enabled them to obtain satisfactory photographs of the flame-front during the "uniform movement," but was not applicable if the speed of the flame was irregular.

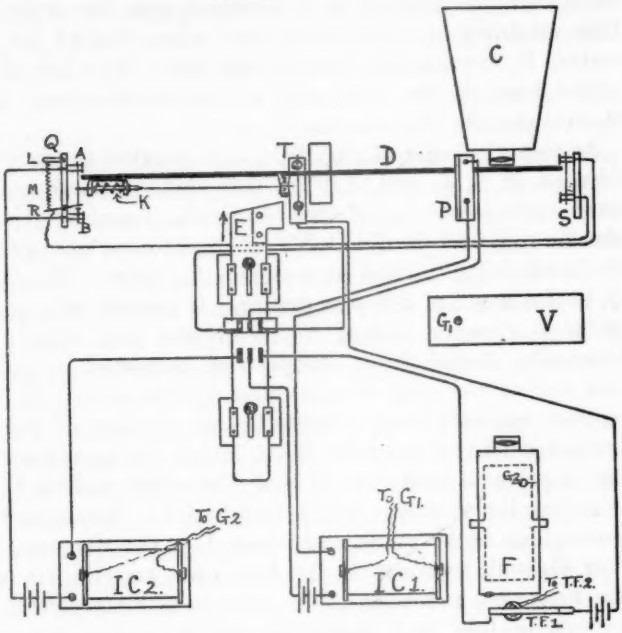
The apparatus to be described has been successfully used to obtain such photographs as were desired, namely, snapshots of flames at any interval of time after their initiation. When the flame is moving (along a tube, for example) a number of snapshots showing consecutive phases of the propagation can be photographed on one plate. This method of flame analysis has given such satisfactory results that the authors have been asked to describe their apparatus in detail, in the belief that it will prove of value to other workers.

The most important element of the apparatus is a revolving shutter, D, Fig. 1, consisting of a steel disk, two metres in circumference, from the periphery of which have been cut 24 windows, each 3 cm. square and spaced at intervals of 15°. This disk is rotated at any desired speed in front of the lens of a camera with a stationary photographic plate, in such a manner that the windows periodically allow light to pass to the lens. According to the character of the flame to be photographed, a few or one only of the windows may be required; the remainder can readily be closed by pasting paper over them. The measurements of the times of the exposures and their synchronisation with the movements of the flame are effected by electrical means.

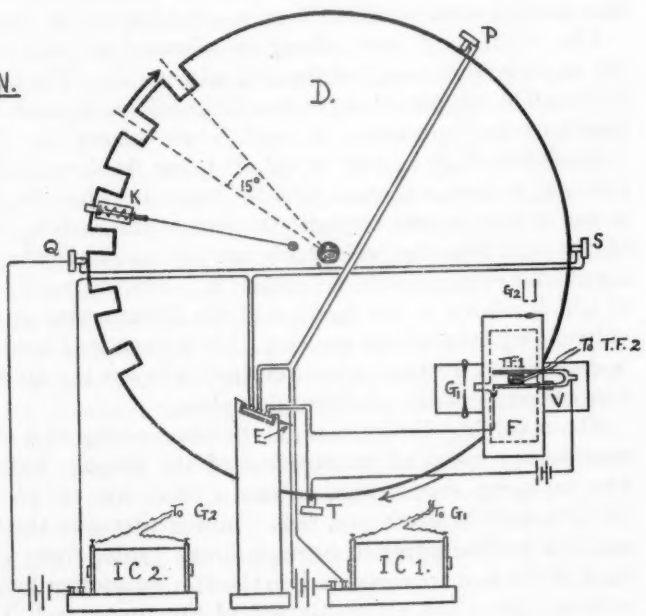
The operation of the several electric circuits is brought about by means of a radial knife, K, held in a light carrier fixed near the periphery of the disk. Normally the knife projects about a centimetre beyond the carrier, but it can be withdrawn, against

FIG. 1.

PLAN.



ELEVATION.



the compression of a light spring, by a thread of cotton which, when taut, is clamped in a terminal near the axle of the disk. This retaining thread can be cut when desired by moving the cutter, E, towards the face of the disk. The act of moving the cutter towards the disk also automatically closes all the three electric circuits that are used.

Astride the edge of the disk, and parallel to its axis, are four stirrups, P, S, T, and Q. The first three of these are identical in form, each consisting of two terminals, 6 cm. apart, mounted on ebonite rod, with flexible leads soldered to the legs of the terminals, the heads being bridged by 5-ampere fuse wire. The fourth stirrup, Q, is of somewhat different design. It consists of a piece of copper strip, R, loosely pinned to an ebonite rod, which carries two terminals, A and B, in the position indicated in plan in Fig. 1. One end of the strip is connected by the spring, M, to a peg, L, so that normally it is drawn by the tension of the spring into contact with the terminal, B. Contact can be prevented by looping a piece of fuse wire round the other end of the strip and clamping the taut wire in the terminal A. Assuming the electrical connexions to be made as indicated in the diagram, current will flow through terminal A, the fuse wire, and the copper strip. If the fuse wire is ruptured, the current is momentarily interrupted by just so long as it takes the spring to draw the released strip into contact with terminal B, so re-establishing the circuit.

The position of each stirrup is adjusted so that its fuse wire lies as close to the edge of the disk as possible. The three stirrups, Q, S, and T, are placed in permanent positions, since their respective functions are constant. Q and S are placed in the positions indicated in Fig. 1, 180° apart, S being fixed so that the radial knife, K, is just in contact with the fuse wire when the first window in the disk is exactly opposite the lens of the camera; the position of T is such that the radial knife has just passed it when the retaining thread engages with the cutter, E. The stirrup P, the function of which relates to the ignition of the inflammable mixture, is the only one without a fixed position. As is explained later, its position is determined by the interval desired between the ignition and the first exposure of the photographic plate.

The revolving film camera, F, besides serving as a chronograph, records the speed of propagation of the flame. The roof of the box enclosing this camera carries a small lens which focusses on the film a short spark gap, G 2. In a similar way the flashes from an electrically-controlled mercury-break tuning-fork, TF 1, at the back of the box are registered on the film by another lens and record a time-scale. The electromagnet of the tuning-fork TF 1 is con-

nected in series with the circuit of a second tuning-fork, TF 2, of the same frequency, vibrating in unison with it, although no flashes appear at the mercury-break of the first fork until the electric circuit of which it forms a part has been completed.

Each of the three electric circuits involved in the apparatus has its own sliding switch on the cradle of the cutter, E. The igniting-circuit for the inflammable mixture comprises a battery in series with a cradle switch, the stirrup P, and the primary of the induction coil, IC 1. The second circuit contains a battery in series with stirrups Q and S, a cradle switch, and the primary of an induction-coil, IC 2. The secondary windings of the coils IC 1 and IC 2 are connected to the spark gaps, G 1 and G 2, respectively, the tremblers of both coils being locked. The third circuit contains a battery in series with stirrup T, a cradle switch, and the mercury-break of the tuning fork, TF 1.

The function of the various circuits will probably be best understood from a description of an experiment. It will be assumed that the radial knife has been withdrawn within the periphery of the disk by its retaining thread, that the cutter is drawn back so that the cradle switches are open, and that the four stirrups are fitted with fuse wire in the manner already described. Only the first six windows in the disk are open. The disk and the revolving drum of the film camera, F, have reached their full speed, the explosion-vessel, V, to be photographed is filled with the required mixture, and the tuning forks are vibrating steadily.

On driving the cutter E sharply forward towards the disk, all three electric circuits are automatically closed, so that the current flows through the primary windings of the two coils and across the mercury-break of the tuning fork, TF 1; the flashes from this mercury-break are registered on the revolving film of the camera F.

The retaining thread of the radial knife having been severed on coming in contact with the razor edge of the cutter, the knife moves outward to its natural position beyond the periphery of the disk, and severs all four fuse-wires in turn.

The rupture, at stirrup Q, of the primary circuit of the coil IC 1 causes a spark to pass across the gap G 2, registering on the revolving film the instant at which one half-revolution of the disk is begun, but, owing to the special form of this stirrup, the electric current is re-established after an instant's delay. Similarly, the rupture of the fuse-wire of stirrup P causes a spark across the gap G 1. This spark ignites the mixture in V and its passage is registered on the revolving film. When the knife, after passing stirrup Q, has moved through 180° (equivalent to 12 windows in the disk), it encounters the fuse-wire of stirrup S, whilst, at the same instant,

the first window in the disk appears opposite the lens of the plate camera, C. The spark which passes across the gap G 2 when the radial knife severs the fuse wire of stirrup S registers on the revolving film the instant at which the first exposure is made, and this coincides with the completion of one half-revolution of the disk. Finally, as the knife severs the wire of stirrup T, the tuning-fork flashes cease.

The film record of the various sparks and of the time-scale supplies all the information necessary to calculate the interval between the time of ignition of the inflammable mixture and the first exposure of the plate, and intervals between successive exposures.

Our thanks are due to the Explosives in Mines Research Committee and to the Safety in Mines Research Board, for whom the work has been carried out, for permission to publish this paper.

SAFETY IN MINES RESEARCH BOARD LABORATORIES,
SHEFFIELD. [*Received, January 28th*, 1925.]

CVIII.—*The Movement of Flame in Closed Vessels.*

By OLIVER COLIGNY DE CHAMPFLEUR ELLIS and RICHARD VERNON WHEELER.

WHEN considering the inflammation of mixtures of methane and air in closed spherical vessels (Wheeler, J., 1918, **113**, 840), it was assumed that, if the ignition of the mixture is exactly at the centre of a sphere, the propagation of flame follows regular concentric spherical surfaces in such a manner that the boundary is reached simultaneously at all points. For, except with very slowly moving flames, or, possibly, in very large vessels, convection currents would not appreciably affect the speed in any particular direction. It was shown experimentally that, with any mixture of methane and air containing more than 7·5 and less than 12·5% of methane, the time taken for flame to travel from the centre of a closed vessel to the top and to the bottom was the same.* Further, it could be deduced from the times taken for the development of the maximum pressures when a series of mixtures of methane and air was inflamed in spheres of 9·75 cm. and 15·6 cm. radius, that (ignoring the initial impetus given by the impulsive discharge used to cause ignition) the speed

* With mixtures containing less than 7·5 and more than 12·5% of methane, in which the rate of propagation of flame is slow, flame reached the bottom of the vessel later than it reached the top by an interval that varied with the methane-content of the mixture.

PLATE 1.

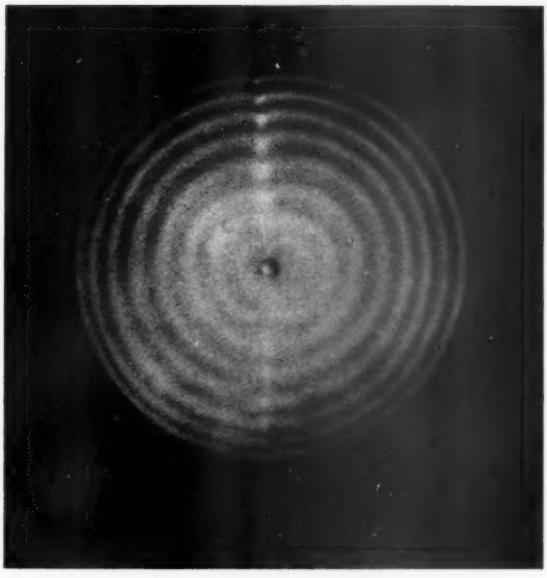


FIG. 1.—*Central ignition.*

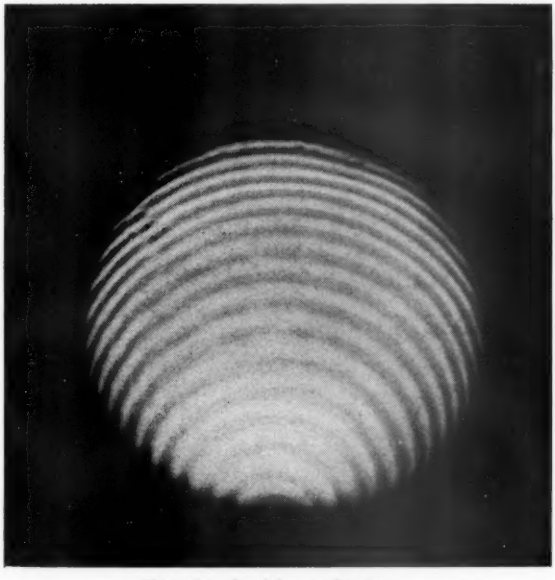


FIG. 2.—*Ignition at bottom.*

Propagation of flame within a closed sphere. Successive intervals of 4·58 milliseconds.

[*To face p.* 765.]

PLATE II.

FIG. 1.—*After* 9·16 *milliseconds.*

FIG. 2.—*After* 22·9 *milliseconds.*

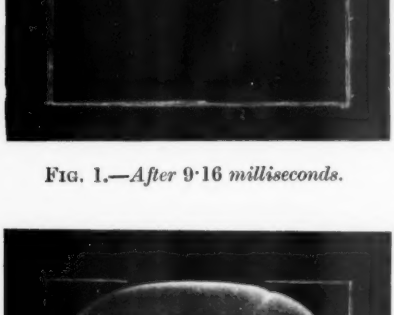


FIG. 3.—*After* 36·44 *milliseconds. Flame just touching sides of cylinder.*

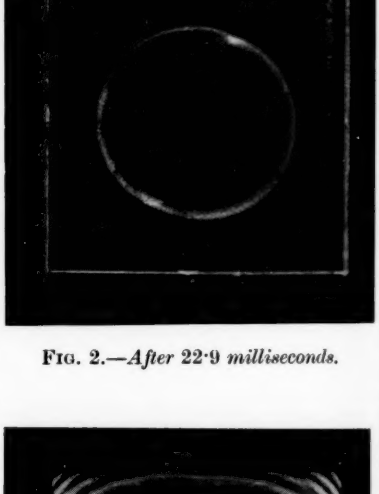


FIG. 4.—*After* 36·64 *milliseconds and subsequently at intervals of* 4·58 *milliseconds.*

Propagation of flame within a closed cylinder. Central ignition.

at which flame travelled from the centre to the walls of the spheres was uniform (*loc. cit.*, p. 852).

We have recently been able to obtain experimental proof of the correctness of these assumptions regarding the manner in which flame spreads from the centre of a closed spherical vessel, by means of the apparatus described elsewhere in this journal (Ellis and Robinson, preceding paper).

Fig. 1, Plate I, is a reproduction of a series of photographs, taken at intervals of 4·58 milliseconds on the same stationary plate, of flame moving in a vertical plane away from the centre of a sphere of glass, 9 cm. in diameter. The duration of exposure of each photograph was 1·69 milliseconds. It will be seen that the flame "follows regular concentric spherical surfaces" and reaches the boundary simultaneously at all points; whilst, so soon as the initial impetus due to the secondary discharge used to ignite the mixture has died away, the speed of the flame becomes uniform. A companion series of photographs of the flame moving in a horizontal plane was identical.

Mallard and le Chatelier (*Ann. Mines*, 1883, [viii], **4**, 379), in connexion with their work on the pressures produced by gaseous explosions, made assumptions (from their time–pressure curves) regarding the movement of flame in a closed cylinder which we can now show to be correct. They used a cylinder the length and diameter of which were equal (17 cm.), and ignited the mixture at the centre. Their description of the manner in which the flame spread from the spark-gap can be freely translated as follows:

"Owing to the unfortunately faulty shape of our explosion-vessel, the propagation of flame assumed two phases. The inflammation, produced at the centre of the cylinder by the spark, is at first propagated away from the point of ignition as a kind of spherical wave which continuously increases in size until it touches the walls of the cylinder. The height of the cylinder being equal to its diameter, the wave (if it remains spherical) touches the sides and the top and bottom plates simultaneously. The second phase in the propagation then begins and continues until the flame reaches the curve of intersection of the end plates with the cylindrical walls.

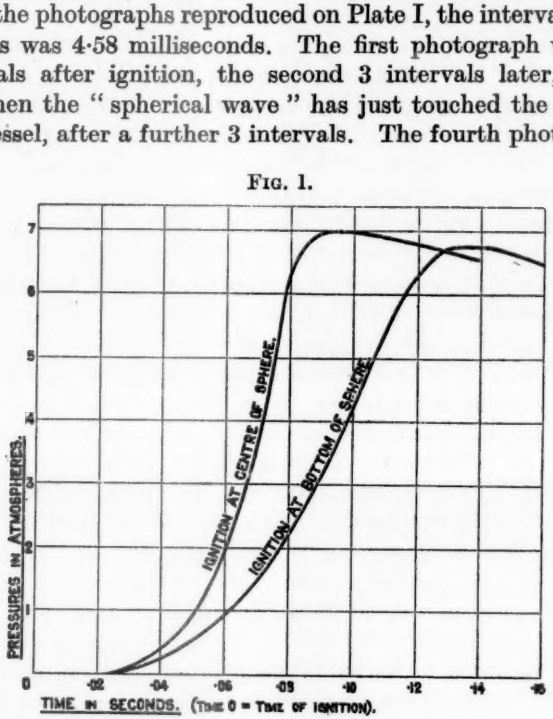
"During the first phase, the propagation takes place without appreciable cooling, since the wave of flame has not yet touched the walls and there is therefore no loss of heat other than that arising from radiation and the small amount due to the abstraction, from the unburnt mixture in contact with the walls of the vessel, of the heat of compression caused by the expansion of the burnt mixture near the centre. Both these causes of loss can be regarded as negligible.

"During the second phase, on the contrary, cooling by the walls

takes place and increases as the propagation proceeds, since the area of the surface of the cylinder in contact with the flame increases."

The correctness of Mallard and le Chatelier's deductions can be judged from the photographs on Plate II, which show separate stages in the propagation of flame, in a vertical plane, from the centre of a glass cylinder 10 cm. long and 10 cm. in diameter. As with the photographs reproduced on Plate I, the interval between exposures was 4·58 milliseconds. The first photograph was taken 2 intervals after ignition, the second 3 intervals later, and the third, when the "spherical wave" has just touched the boundary of the vessel, after a further 3 intervals. The fourth photograph is

FIG. 1.



a composite one, showing successive stages, 8, 9, 10, and 11 intervals after ignition, which represent the second phase of the propagation, when the flame is squeezing itself into the "corners" of the cylinder. The boundary of the vessel is shown in each instance by white lines drawn on the photograph. It will be noticed that the centre of the vessel is re-illuminated after the flame has reached the sides. This phenomenon will be discussed in a later communication.

The extent to which cooling of the flame by the walls of a spherical vessel can occur when ignition is not central is illustrated in Fig. 2, Plate I. Ignition was at a spark-gap between electrodes which just passed through the walls of the sphere at the bottom, and the photographs were taken, in a vertical plane, at intervals of 4·58 milliseconds. The inflammable mixture had the same composition as in

the experiment illustrated in Fig. 1, and the intensity of the source of ignition was approximately the same.

It will be understood that cooling by the walls of the vessel, and consequent retardation of the flame, can affect not only the maximum pressure that a given mixture can produce when it is inflamed, but also the rate of development of pressure; so that when attempting to interpret the character of time–pressure curves obtained from gaseous explosions in closed vessels due consideration must be paid to the shape of the vessels and to the position of the point of ignition. The curves in the text (Fig. 1) illustrate this. Both were obtained by the inflammation of mixtures of methane and air of the same composition (10·15% of methane) in a spherical explosion-vessel of 4 litres capacity, similar in design to that described in J., 1918, 113, 854. In one experiment, ignition of the mixture was at the centre of the sphere; in the other it was at the bottom. In the latter, the rate of development of pressure is considerably retarded and the maximum pressure attained is less.

Our thanks are due to the Explosives in Mines Research Committee and to the Safety in Mines Research Board for permission to publish this paper, which should be regarded as preliminary to a detailed study of the movement of flame in closed vessels.

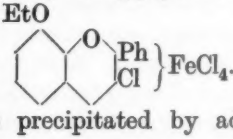
SAFETY IN MINES RESEARCH BOARD LABORATORIES,
SHEFFIELD. [*Received, January 28th*, 1925.]

NOTES.

3-*Chlorobenzopyrylium Derivatives*. By LESLIE RANDAL RIDGWAY and ROBERT ROBINSON.

WE have recently shown (J., 1924, 125, 214) that the condensation of 2-hydroxy-3-ethoxybenzaldehyde and acetophenone or ω-bromoacetophenone under the influence of hydrogen chloride leads to 8-ethoxy-2-phenylbenzopyrylium chloride. Reduction does not occur, however, when ω-chloroacetophenone and ω-chloroacetylanisole are condensed in a similar manner with 2-hydroxy-3-ethoxybenzaldehyde. Characteristic pyrylium salts bearing a chlorine atom as a substituent in position 3 are so obtained.

3-*Chloro*-8-*ethoxy*-2-*phenylbenzopyrylium Ferrichloride*,



—A *ferrichloride* was precipitated by addition of concentrated

hydroferrichloric acid to a mixture of ω-chloroacetophenone (2 g.), 2-hydroxy-3-ethoxybenzaldehyde (2 g.), and glacial acetic acid (10 c.c.) which had been saturated with hydrogen chloride during 5 hours. The derivative was washed with ether and thrice crystallised from acetic acid (Found : C = 42·5 ; H = 3·2. $C_{17}H_{14}O_2Cl_5Fe$ requires C = 42·2; H = 2·9%), 1·0 g. of maroon prisms, m. p. 155°, soluble in alcohol to a yellow and in chloroform to an orange solution, was obtained. In a similar manner, but in doubled yield, ω-chloroacetylanisole gave *3-chloro-4′-methoxy-8-ethoxy-2-phenylbenzopyrylium ferrichloride*, which crystallises from acetic acid in highly lustrous, long, rectangular, brick-red plates, m. p. 150° (Found : C = 42·1; H = 3·3; Cl = 34·9. $C_{18}H_{16}O_3Cl_5Fe$ requires C = 42·1; H = 3·1; Cl = 34·6%). Each of these ferrichlorides readily yields a colourless pseudo-base from which the yellow oxonium salt can be regenerated by the action of mineral acids.—The University, Manchester. [*Received, January* 31*st*, 1925.]

A Qualitative Test for Weak Bases. By Robert Robinson.

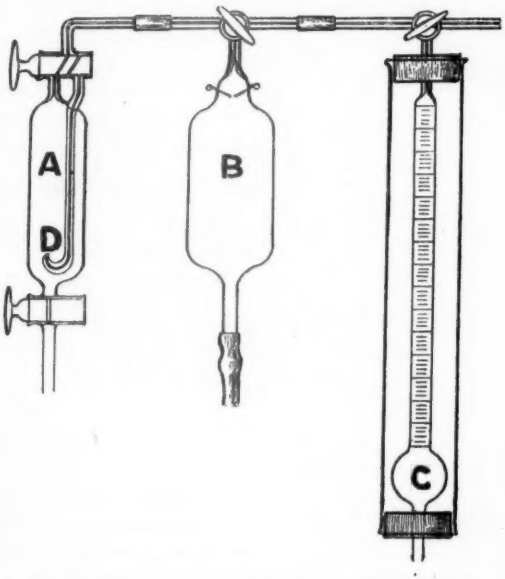
A solution of hydroferrichloric acid made by saturating concentrated hydrochloric acid with ordinary crystallised ferric chloride is added to a solution of the substance to be tested in light petroleum (b. p. 40—60°). Three layers are often produced : the lowest is an aqueous solution of ferric chloride and hydrochloric acid much more dilute than the reagent; the green or brown middle layer contains the weak base, ferric chloride, and hydrogen chloride; the top layer consists chiefly of light petroleum. This behaviour is clearly due to the formation of ferrichlorides and is exhibited by the majority of carbon compounds, containing oxygen, nitrogen or sulphur, that are sufficiently readily soluble in light petroleum. Positive results are obtained with all simple alcohols except methyl and ethyl alcohols (which are too soluble in water), *e.g.*, *iso*amyl alcohol, benzyl alcohol, *cyclo*hexanol; with aliphatic ethers, *e.g.*, diethyl ether, di*iso*amyl ether; with esters, *e.g.*, ethyl acetate, ethyl benzoate; with ketones, *e.g.*, *cyclo*hexanone, acetophenone; with aldehydes, *e.g.*, *n*-heptaldehyde, benzaldehyde; with phenol ethers, *e.g.*, anisole, veratrole; with nitro-compounds, *e.g.*, nitromethane, nitrobenzene; with nitriles, *e.g.*, acetonitrile, phenylacetonitrile; with thio-ethers, *e.g.*, diethyl sulphide; and with many other classes of compounds. More than two hundred cases have been tried and the following exceptions noted : carboxylic acids, acid chlorides (but not anhydrides, amides, or ester chlorides,

e.g., ethyl chloroformate gives positive results), thiophen, safrole, diphenyl ether. It is remarkable that the methylenedioxy-group should not confer oxonium character, but the other exceptions are easily understood, and diphenyl ether may be compared in this respect with diphenylamine.

Naturally, since water is present in the system, there is a certain minimum strength of a base below which this test is not diagnostic. Some practical applications may be indicated. (1) Traces of oxygenated and nitrogenous compounds may be removed from hydrocarbons by washing with hydroferrichloric acid. (2) Camphor oil contains safrole and camphor, and when a mixture of these substances is dissolved in light petroleum and hydroferrichloric acid is added, a green middle layer can be separated which gives solid camphor on treatment with water. Safrole remains in the light petroleum solution.—THE UNIVERSITY, MANCHESTER. [*Received, January* 31*st*, 1925.]

A New Portable Apparatus for the Analysis of Illuminating and Other Gases. By HUMPHREY DESMOND MURRAY.

THIS apparatus differs from previous modifications in that only one pipette is employed, and each absorbent is sucked up into the latter as required. The usual gas burette, C, is attached above to a three-way tap, one conduit of which leads to the external gas connexion, the other to the intermediate container, B, through a second three-way tap. The other conduit of the container is attached to the gas pipette, A, which has two alternative leads, so that the gas may be injected through the jet, D, and withdrawn through the upper tube. The container B is provided with a mercury reservoir attached to its lower end by a piece of flexible



tubing. Before use, B is filled with mercury and C with some containing liquid, which in most cases may be slightly acidified water. If the absorbent does not act rapidly upon rubber tubing, the lower lead-in tube of A is attached thereby to the vessel containing the absorbent. If the use of rubber is not permissible, the lead-in tube of A is immersed directly in the absorbent, which is drawn into the pipette by lowering the mercury in B. The gas is then passed through the absorbent in a fine stream of bubbles and returned to the burette, where its contraction is measured. For the analysis of gaseous mixtures containing such gases as hydrogen and methane, a measured volume of air or oxygen is added to the gas in C, and the mixture passed into B, exploded, and returned to C, where any alteration in volume may be measured. Any products of the explosion can be measured as above described by absorption with suitable reagents in A. In the case of absorptions requiring the use of two absorbents, the second may be drawn into B. If, when bromine water is to be used, a layer of caustic potash is introduced above the mercury in B, the gas after treatment in the pipette may be passed first into B, where the bromine fumes are removed, and then into the burette. The apparatus permits of clean and rapid analyses, and since it is never permanently charged with reagent it is very portable.—IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY, SOUTH KENSINGTON. [*Received, February 2nd*, 1925.]